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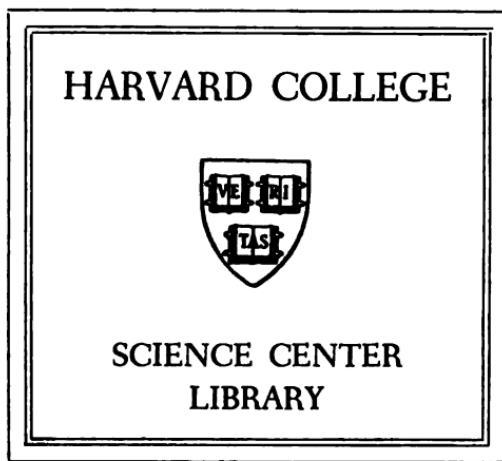
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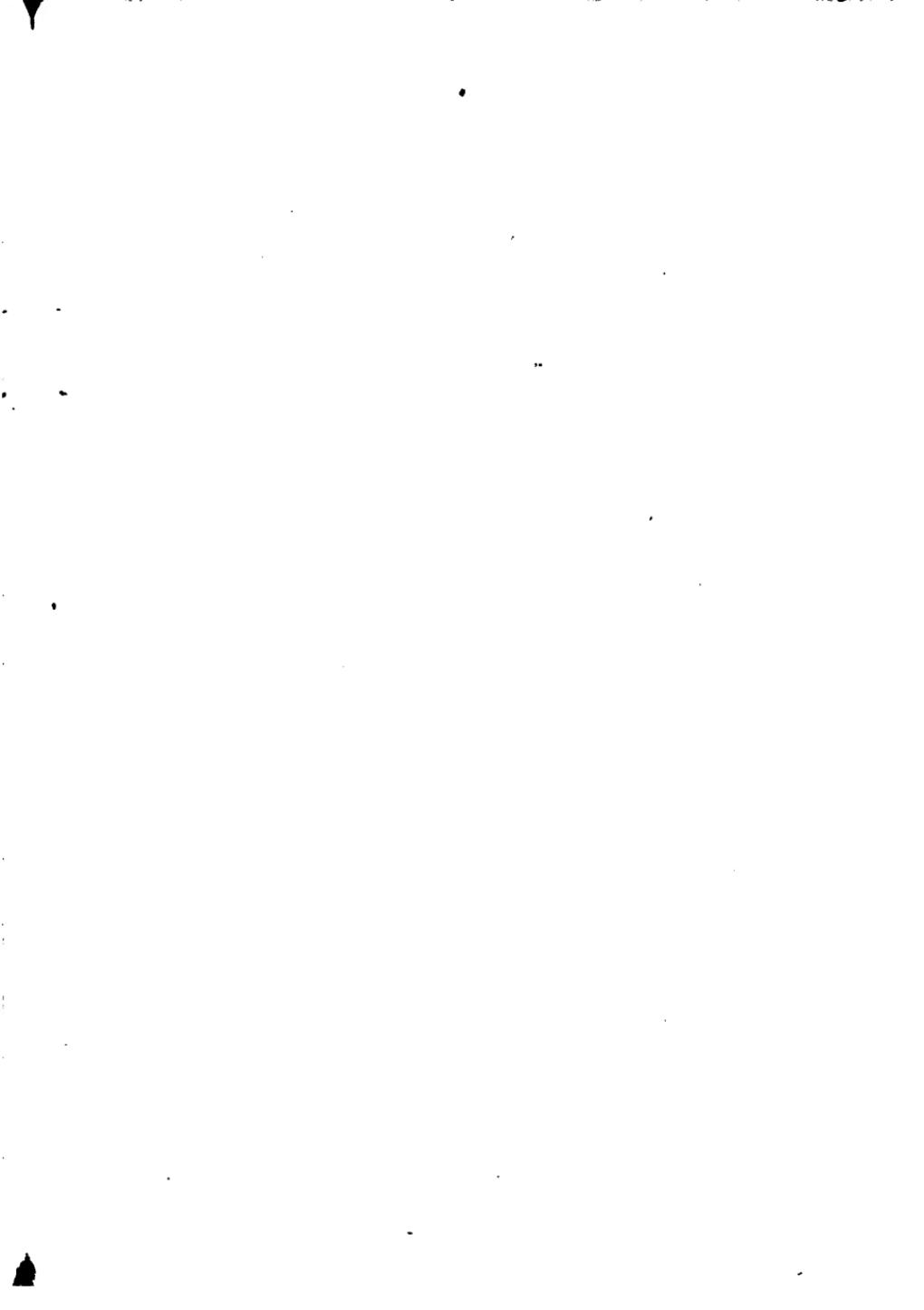
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ANTOINE LAURENT LAVOISIER

1743-1794

THE CELEBRATED FRENCH CHEMIST WHO LAID THE FOUNDATIONS OF CHEMISTRY

# DESCRIPTIVE CHEMISTRY

BY

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## PREFACE.

THIS book is intended for teachers who wish to emphasize the facts, laws, theories, and applications of chemistry. It is divided into two parts. Part I contains the text, together with exercises and problems. Part II contains the experiments. The text has been selected and arranged with special reference to the needs of teachers as well as to the capacity of students. The experiments have been prepared to meet the needs of those schools in which the laboratory facilities are limited or the time for chemistry is short.

The point of view differs from that in the author's "Experimental Chemistry," but the spirit is the same. The two books are companion volumes, though of course they can be used independently. The cordial reception given the "Experimental Chemistry" shows that many teachers are emphasizing the experimental side of chemistry. These teachers will find Part I of the "Descriptive Chemistry" a serviceable companion book both in the laboratory and class room. It has been bound as a separate volume to meet such a use.

Solutions of problems, answers to some of the exercises, and references to the literature have been put in a separate *Teacher's Handbook*.

The manuscript has been read by Dr. William B. Schober, Lehigh University, Bethlehem, Pennsylvania; Mr. Franklin T. Kurt, Chauncey Hall School, Boston, Massachusetts; and Mr. George M. Turner, Masten Park High School, Buffalo, New York. The chapters on theory were also read by Dr. Alexander Smith of the University of Chicago, and the chapters on carbon by Dr. James F. Norris of the Massachusetts Institute of Technology. The proof has been read by Dr. E. H. Kraus, High School, Syracuse, New York; Professor E. S. Babcock, Alfred University, Alfred, New York; and Mr. E. R. Whitney, High School, Binghamton, New York. The author is grateful to these teachers for their criticism, but he assumes all responsibility for any errors which may be detected.

L. C. N.

LOWELL, MASS.,  
May, 1903.

## PREFACE TO REVISED EDITION

ALL the general features of the first edition which teachers universally commended have been retained in the revised edition. The chapters dealing with the theory of chemistry have undergone revision. Additional applications of the theory of electrolytic dissociation have been made in several instances, especially in the chapter on Acids, Bases, and Salts. Radium, radio-activity, hydrolysis, vapor pressure, and other new topics have been inserted. Numerical data have been revised and several tables have been rewritten.

Several experiments in Part II have been modified, a few have been entirely rewritten, and some new ones have been introduced. These modifications, however, have not destroyed the serviceableness and simplicity of this part of the book — characteristics which have received the hearty approval of teachers.

Opportunity has been taken at this time to incorporate the suggestions of many teachers who have generously contributed from their experience.

The author deeply appreciates the cordial reception given the first edition of this book and the continued confidence expressed by teachers who have used it since the publication. He trusts the revised edition will meet with equal favor and will speedily find a larger field of usefulness.

L. C. N.

BOSTON, Mass.,  
May, 1909.

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**PART I**

**DESCRIPTIVE**

**CHEMISTRY**



# DESCRIPTIVE CHEMISTRY.

---

## CHAPTER I.

### INTRODUCTION.

CHEMISTRY is a branch of natural science. It deals with the properties of matter, the changes which affect the composition of matter, with numerous laws and theories, and with the manufacture of a vast number of different substances indispensable to the welfare of mankind.

**Properties of Matter.**—Different substances are recognized and distinguished by their **properties**. Color, odor, taste, weight, and solubility are familiar properties; but to these must be added behavior with heat, light, and electricity, and especially the action of different kinds of matter upon each other.

**Physical and Chemical Changes.**—Observation shows that the properties of matter can be changed. Sometimes the change is only temporary, as in the freezing of water, or in the melting of iron. Such changes are called **physical changes**. But often the change is permanent, as in the burning of coal, or the digestion of food. Such changes are called **chemical changes**. In physical changes the original properties reappear after the cause of the change has been removed. But chemical changes

## Descriptive Chemistry.

affect the essential nature of a substance. They are fundamental. Removal of the cause of a chemical change does not restore the original properties of the substance. Thus, coal is readily changed into ashes and invisible gases, but the ashes and gases do not reunite into coal after the heat has been removed. Another essential characteristic of chemical changes is the formation of one or more kinds of matter different from the original substance. Thus, water may be decomposed by electricity into two gases—hydrogen and oxygen. This is a chemical change, because (1) the water has disappeared, its identity is lost, it has been permanently changed, and (2) other kinds of matter have been formed, which are totally unlike water.  
**Chemistry is largely a study of chemical changes.**

The different changes which matter undergoes furnish a convenient basis for the classification of properties. Thus, we call **physical properties** those which accompany physical changes; while **chemical properties** require a chemical change for their manifestation. Thus, the color, luster, specific gravity, melting point, and capacity to conduct electricity are physical properties of copper; but it displays chemical properties when it is heated, or when acted upon by acids, sulphur, and other substances.

Examples of simple physical changes are the formation of ice or steam from water, the electrification of a copper trolley wire, the production of colors in the sky, the magnetization of iron in a dynamo or magnet, and the melting of iron in a foundry. Familiar chemical changes are the rusting of iron, the growth of plants, the burning of oil in a lamp, the decay of fruit, and the souring of milk.

Chemical changes are often complex. In many instances they are caused by heat, and usually they produce heat. In general, the velocity of chemical change increases with rise of temperature. Light induces chemical

changes, as in growing plants and on photographic plates. Electricity is involved in many chemical changes, a vast industry having recently grown up in this field. Contact is necessary for chemical change, and many substances must be pressed together, intimately mixed, or dissolved before they will interact.

Physical and chemical changes are closely related. They usually accompany each other, and are often inseparable. If the essential change in a substance or substances is chemical, then the substances are said to undergo **chemical action**. Very often the chemical action involves several substances. The substances are then said to **interact** or **react**, and the series of changes is called a **reaction**. Thus, when zinc is added to nitric acid, the chemical action which occurs is manifested by the formation of a brown gas and the disappearance of the zinc. The zinc and acid interact, and the chemical changes can be classified as due to the reaction between zinc and nitric acid.

**Classes of Chemical Action.** — There are four general kinds of chemical action. (1) **Analysis or decomposition** is the separation of matter into its components. Thus, heat decomposes wood, and the juices of our bodies decompose food. (2) **Synthesis or combination** is the union of different kinds, or sometimes the same kind, of matter. For example, the gases, hydrogen and oxygen, may be made to unite and form water by passing an electric spark through them. (3) **Substitution** is the replacement of one kind of matter by another. When zinc is added to hydrochloric acid, the hydrogen leaves the acid, and zinc takes its place. (4) Sometimes parts of different substances exchange places; this kind of change is called **metathesis or double decomposition**. If silver nitrate is

added to hydrochloric acid, the silver and hydrogen exchange places, forming silver chloride and nitric acid. These four kinds of chemical changes will be fully illustrated and studied in the succeeding pages.

**Chemical Energy.**—We learn in physics that heat, light, and electricity are different forms of energy. They produce special changes. It is also possible to transform the different kinds of energy into each other. Thus, electricity is generated from the heat liberated by burning coal, and electricity in turn may be transformed into light. In chemistry we study another kind of energy, called **chemical energy**, chemical attraction, or chemism. This is the immediate agent involved in chemical change. Combination and decomposition are due to its operation. Chemical energy may be transformed into light, electricity, and heat, and *vice versa*. Appreciable heat often accompanies chemical changes, and we shall have many illustrations of the intimate relation between heat and chemical energy. Electricity is produced in an electric battery by chemical action. Light is one result of the chemical action called combustion or burning. In fact, every chemical change is accompanied by an energy change of some kind, and in such transformations all the energy can be accounted for, none is lost or gained.

Chemical energy is an essential factor in all chemical changes, but we know little or nothing of its nature. We can only study its results and its manner of action.

**Conservation of Matter.**—In chemical changes matter is not created or destroyed. It is often transformed, and apparently lost, but the total weight of the substances participating in any chemical change is always the same. The fact that matter is indestructible was first demon-

strated by the French chemist, Lavoisier (1743-1794), and countless observers have since shown that it is a fundamental law of chemistry. The law is called the **Law of the Conservation of Matter**, and is often stated thus:—

*No weight is lost or gained in a chemical change.*

**Chemical Elements.**—Study of the constitution of matter shows that some kinds can be decomposed into substances totally unlike the original matter. Water, for example, is easily decomposed into the gases, hydrogen and oxygen, which are entirely different from water. But it is impossible by any known process to obtain from some kinds of matter substances which have simpler properties than the original substance. Thus, neither oxygen nor hydrogen can be decomposed by any known means. Iron and the familiar metals likewise cannot be divided chemically into two or more substances, nor can they be transformed into each other. They are fundamental substances. We can add other substances to them, but we cannot get simpler substances from them, nor can we transform them into simpler substances. Iron contains nothing but iron. The substances which have such simple properties and at present defy decomposition and transformation are called the **chemical elements**.

It would follow from this traditional definition that the elements are the primary forms of matter, so to speak, and are chiefly characterized by stability. This is true of most elements, as far as we know. But our inability to decompose elements does not necessarily mean that they are immutable under all conditions. Indeed, their instability is shown by the spontaneous decomposition of certain elements (see Radioactivity).

Each element is designated by a symbol, which is an abbreviation of its name. The following is an alphabetical —

# Descriptive Chemistry.

**TABLE OF THE IMPORTANT ELEMENTS.**

NAME.	SYMBOL.	NAME.	SYMBOL.
Aluminium . . . . .	Al	Lead . . . . .	Pb
Antimony . . . . .	Sb	Lithium . . . . .	Li
Arsenic . . . . .	As	Magnesium . . . . .	Mg
Barium . . . . .	Ba	Manganese . . . . .	Mn
Bismuth . . . . .	Bi	Mercury . . . . .	Hg
Boron . . . . .	B	Nickel . . . . .	Ni
Bromine . . . . .	Br	Nitrogen . . . . .	N
Cadmium . . . . .	Cd	Oxygen . . . . .	O
Calcium . . . . .	Ca	Phosphorus . . . . .	P
Carbon . . . . .	C	Platinum . . . . .	Pt
Chlorine . . . . .	Cl	Potassium . . . . .	K
Chromium . . . . .	Cr	Silicon . . . . .	Si
Cobalt . . . . .	Co	Silver . . . . .	Ag
Copper . . . . .	Cu	Sodium . . . . .	Na
Fluorine . . . . .	F	Strontium . . . . .	Sr
Gold . . . . .	Au	Sulphur . . . . .	S
Hydrogen . . . . .	H	Tin . . . . .	Sn
Iodine . . . . .	I	Zinc . . . . .	Zn
Iron . . . . .	Fe		

Of the above elements only eight are abundant in the earth's crust, as may be seen by a —

**TABLE OF THE APPROXIMATE COMPOSITION OF THE EARTH'S CRUST  
(BY WEIGHT).**

ELEMENT.	PER CENT.
Oxygen . . . . .	47.07
Silicon . . . . .	28.06
Aluminium . . . . .	7.90
Iron . . . . .	4.43
Calcium . . . . .	3.44
Magnesium . . . . .	2.40
Potassium . . . . .	2.45
Sodium . . . . .	2.43
Total . . . . .	98.18

The atmosphere contains about 20 per cent of oxygen and 79 per cent of nitrogen in the free state. The ocean contains about 86 per cent of oxygen, 11 per cent of hydrogen, and 2 per cent of chlorine in combined states. It is clear that the globe, as we know it, is made up of a very few elements.

Many of the familiar metals are elements, *e.g.* lead, zinc, tin, copper, iron, gold, and silver. Other elements besides the metals are solids, such as sulphur, carbon, and phosphorus; two are liquid, viz. bromine and mercury; while several are the common gases, oxygen, nitrogen, and hydrogen. Many are important simply because they are combined with other elements, especially silicon, which is found in most rocks, and calcium, which is a component of limestone.

The following is a —

TABLE OF THE UNCOMMON ELEMENTS.

NAME.	SYMBOL.	NAME.	SYMBOL.
Argon . . . . .	A	Prasedymium . . . . .	Pr
Beryllium . . . . .	Be	Rhodium . . . . .	Rh
Cæsium . . . . .	Cs	Rubidium . . . . .	Rb
Cerium . . . . .	Ce	Ruthenium . . . . .	Ru
Erbium . . . . .	Er	Samarium . . . . .	Sm
Gallium . . . . .	Ga	Scandium . . . . .	Sc
Germanium . . . . .	Ge	Selenium . . . . .	Se
Glucinum . . . . .	Gl	Tantalum . . . . .	Ta
Helium . . . . .	He	Tellurium . . . . .	Te
Indium . . . . .	In	Thallium . . . . .	Tl
Iridium . . . . .	Ir	Thorium . . . . .	Th
Krypton . . . . .	Kr	Titanium . . . . .	Ti
Lanthanum . . . . .	La	Tungsten . . . . .	W
Molybdenum . . . . .	Mo	Uranium . . . . .	U
Neodymium . . . . .	Nd	Vanadium . . . . .	V
Neon . . . . .	Ne	Xenon . . . . .	Xe
Niobium . . . . .	Nb	Ytterbium . . . . .	Yb
Osmium . . . . .	Os	Yttrium . . . . .	Yt
Palladium . . . . .	Pd	Zirconium . . . . .	Zr

**Chemical Symbols** are usually the first letter of the name of the element. Thus, O is the symbol of oxygen, H of hydrogen, N of nitrogen. Since several elements have the same initial letter, the symbol of some elements contains two letters. Thus, C represents carbon, while the symbol of calcium is Ca, of chlorine Cl, of chromium Cr, and of copper Cu. The symbols of several elements, especially the metals so long known, are derived from their Latin names, as may be seen from a —

TABLE OF LATIN SYMBOLS.

ELEMENT.	LATIN NAME.	SYMBOL.	ELEMENT.	LATIN NAME.	SYMBOL.
Antimony	Stibium	Sb	Mercury	Hydrargyrum	Hg
Copper	Cuprum	Cu	Potassium	Kalium	K
Gold	Aurum	Au	Silver	Argentum	Ag
Iron	Ferrum	Fe	Sodium	Natrium	Na
Lead	Plumbum	Pb	Tin	Stannum	Sn

Symbols always begin with a capital, and are not followed by a period. They should be learned by actual use. Their significance will be explained in later chapters.

**Chemical Compounds.** — When elements unite with each other the product of the union is a **chemical compound**. The elements which make up a chemical compound are called **components**. Chemical compounds have three essential characteristics. (1) Their components are held together by chemical attraction. The hydrogen and oxygen, which are the components of water, cannot be separated unless their attraction for each other is overcome by heat, electricity, or some other agent. (2) In any given chemical compound the components are always in

the same ratio. Thus, pure common salt, however prepared or wherever found, always contains 39.32 per cent of sodium and 60.68 per cent of chlorine. So also water always contains eight parts (by weight) of oxygen and one of hydrogen. Facts similar to these might be given covering all cases examined. Such facts illustrate the general principle that chemical action proceeds according to laws. (3) In chemical compounds the identity of the components is lost. Thus, the red metal, copper, the yellow solid, sulphur, and the invisible gas, oxygen, are the components of the blue solid, copper sulphate.

Chemical compounds must not be confused with *mixtures*. The parts of a mixture may vary in nature and in proportion; they are also held together loosely, and may often be separated by some mechanical operation, as filtering or sifting. A mixture, too, often has properties similar to its parts.

#### EXERCISES.<sup>1</sup>

1. State three properties of (a) glass, (b) wood, (c) water, (d) paper, (e) air.
2. Give three illustrations of (a) physical changes and (b) chemical changes occurring in everyday life.
3. Are the following changes physical or chemical? (a) Burning of wood, (b) melting of butter, (c) freezing an ice-cream mixture, (d) weathering (*i.e.* decay) of granite, (e) tarnishing of brass and other metals, (f) formation of snow, (g) developing a photographic plate, (h) seasoning of wood, (i) formation of dew, (j) disappearance of a fog.
4. What aids and what retards chemical change? What often accompanies it?
5. What physical change accompanies (a) the burning of coal, (b) the action of an electric battery, (c) the burning of a match?
6. Give an illustration of the transformation of chemical energy into heat, light, or electricity.
7. State the law of the conservation of matter.

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<sup>1</sup> These exercises are intended for review work.

## Descriptive Chemistry.

8. (a) Name five elements with which you are familiar. (b) Name the eight most abundant elements in the earth's crust in their order.
9. What common metals are elements?
10. How do elements and compounds essentially differ? Could you prepare (a) a compound from elements, (b) elements from a compound, and (c) elements from elements?
11. Define (a) chemistry, (b) physical change, (c) chemical change, (d) chemical action, (e) analysis, (f) synthesis, (g) metathesis, (h) substitution, (i) element, (j) compound, (k) mixture, (l) symbol.
12. Review or learn the metric system (see Appendix, § 1).

### PROBLEMS.

Perform the problems in the Appendix, § 1.

## CHAPTER II.

### OXYGEN.

**Oxygen** has played an important part in the development of chemistry, and is an appropriate element with which to begin a systematic study of this science.

**Occurrence.**—Oxygen is the most abundant and widely distributed of the elements. Mixed with nitrogen and a few other gases, it forms one fifth (by volume) of the atmosphere. Combined with hydrogen, it constitutes eight ninths (by weight) of water; combined with silicon and certain metals, it makes up nearly half of the earth's crust; while compounds of oxygen, carbon, and hydrogen form a large part of animal and vegetable matter. Starch, for example, which is a constituent of all plants, contains about 50 per cent oxygen.

**Preparation.**—Oxygen may be prepared from its compounds or from air. It was first prepared by decomposing a red compound of oxygen and mercury. When heated in a hard glass tube, this compound decomposes into oxygen and mercury; the oxygen is collected over water in a pneumatic trough, and the mercury condenses as globules or a film on the upper part of the tube. This experiment is historically interesting, because it was first performed by Priestley, the discoverer of oxygen.

The gas is often prepared by decomposing potassium chlorate—a compound of oxygen, chlorine, and potassium. Heated to a rather high temperature, the potassium chlo-

rate passes through a series of changes; as a final result, the oxygen is set free, and potassium chloride, a white solid, remains behind.

Oxygen is most conveniently prepared by heating a mixture of potassium chlorate and manganese dioxide in a glass or metal vessel. The gas is liberated freely from this mixture at a lower temperature than when either compound is heated alone.

The manganese dioxide may be recovered unchanged at the close of the experiment. It takes some part in the chemical changes, but just what is not definitely known. It has been suggested that the manganese dioxide combines at first with oxygen, thereby forming another compound of manganese richer in oxygen than the dioxide, but so unstable that when heated it yields oxygen and manganese dioxide.

Large quantities of oxygen may be prepared by heating a mixture of potassium chlorate and manganese dioxide in a copper or iron retort. Other commercial processes are used. In Brin's process, which is operated largely in England, purified air is forced by a pump over barium oxide heated to  $700^{\circ}\text{C}.$ ,<sup>1</sup> thereby forming barium dioxide. The air supply is then cut off, and the pressure in the retorts reduced by reversing the pump. This operation changes the barium dioxide into barium oxide and oxygen. The gas is drawn off into a reservoir. The process is then repeated. A kilogram of barium oxide yields about ten liters of oxygen at a single operation.<sup>2</sup>

Oxygen can be prepared from liquid air (see Liquid Air). By evaporation at the ordinary temperature and pressure, the nitrogen escapes from the liquid air more rapidly than the oxygen, leaving finally a liquid which is nearly pure oxygen. Unlimited quantities of oxygen may thus be cheaply prepared from the air.

**Properties.**—Oxygen gas has no color, odor, or taste. It is slightly heavier than air. It is somewhat soluble in

<sup>1</sup> C. is the abbreviation of "centigrade," which is the name of the thermometer used in science. According to this thermometer water boils at  $100^{\circ}$  and freezes at  $0^{\circ}$  (see Appendix, § 2).

<sup>2</sup> "Kilogram" and "liter" are denominations of the Metric System of Weights and Measures. This system should be learned or reviewed (see Appendix, § 1).

water, but the presence of even a small proportion in water is exceedingly important. Fish die in water containing no oxygen; and the oxygen absorbed by flowing water helps keep it free from organic matter. (See Decay, below.)

The density of oxygen gas is 1.105 (air = 1). One hundred liters of water dissolve only about three liters of oxygen under ordinary conditions.

The chemical activity of oxygen is its most striking property. It combines with all the other elements except fluorine, bromine, and the inert gases recently discovered in the atmosphere. With most of them the union is direct, and is often accompanied by light and heat, though the temperature at which combination occurs varies between wide limits. At the ordinary temperature it unites with phosphorus, as may be seen by the glow and fumes when the end of a match is rubbed, especially in a dark room. Metals, such as iron, lead, zinc, and copper, tarnish or rust easily, *i.e.* they combine with the oxygen of the air. The chemical activity of oxygen at high temperatures is readily shown by putting burning substances into it. All burn vividly in oxygen.

When a glowing stick of wood is put into oxygen, the stick instantly bursts into a flame; and if left in the oxygen, the wood continues to burn brightly until the gas is exhausted. If glowing charcoal is put into oxygen, the charcoal burns violently, and throws off showers of sparks. Sulphur burns in air with a small, blue flame, but in oxygen the flame is much larger and brighter. The flame in both cases is accompanied by fumes which smell like a burning sulphur match. Iron wire does not burn in air, but if the end is coated with burning sulphur and then put into oxygen, the wire burns vividly, throwing off a shower of sparks; when the flame has disappeared, a globule of red-hot iron is often seen on the end of the wire; and sometimes the inside of the bottle is coated with a reddish powder, which is mainly a compound

of iron and oxygen. Iron and oxygen combine at a higher temperature than do sulphur and oxygen, so sulphur is used to set fire to the iron. On the other hand, if lighted magnesium is put into oxygen, the burning metal instantly becomes surrounded with a dazzling flame, and burns rapidly to a white powder, thus showing that the temperature at which it combines with oxygen is much lower than that required by iron.

**Oxidation.**—When sulphur, iron, magnesium, and carbon (in wood and charcoal), and other elements burn in oxygen, they combine with it. This chemical change is called **oxidation**.

The fact that oxidation is merely a combining with oxygen may be easily verified. It has been repeatedly shown that oxygen is one constituent of all the products formed by burning substances in that gas. Thus, carbon forms an invisible gas called carbon dioxide, which is a compound of carbon and oxygen. Similarly, sulphur, iron, and magnesium form compounds of these elements and oxygen. These facts may be further verified by a simple experiment. If mercury is heated, it gains in weight, and red particles collect on its surface; but if it is protected from the air by some coating and then heated, there is no gain in weight and no evidence of the red product. Therefore, when the exposed mercury is heated, something from the air must be added to it. Now, if the red substance is collected and heated in a glass tube, mercury and oxygen are the only products. Hence, the exposed mercury, when heated, must have combined with the oxygen of the air.

Oxidation is not always rapid enough to produce light and appreciable heat. Iron and other metals rust, and wood decays slowly, but both processes are mainly oxidation. Sometimes oxidation develops considerable heat. Thus, oily rags, piles of hay, and heaps of coal often take fire unexpectedly because of the continued oxidation. Such oxidation is often called spontaneous combustion.

Substances which give up oxygen readily are called **oxidizing agents**. Potassium chlorate is used in fireworks for this purpose, and potassium nitrate acts similarly in gunpowder. In the process of oxidation, oxidizing agents

lose oxygen, and are said to undergo **reduction** — a process which will be more fully described in the next chapter.

**Oxides** are formed when oxygen combines with other elements. There are many oxides, and their names express in a general way their composition. Oxides of different elements are distinguished by placing the name of the element (or a slight modification of it) before the word *oxide*, e.g. magnesium oxide, lead oxide, zinc oxide. Sometimes di-, or a similar numerical syllable, is prefixed to the word *oxide*, e.g. carbon dioxide, manganese dioxide, sulphur trioxide, phosphorus pentoxide. The significance of the prefix is explained in Chapter VII.

**Combustion**, in a narrow sense, is rapid oxidation, which is always accompanied by light and heat. Popularly, combustion means fire or burning, and substances which burn easily are called combustible. Oxygen is essential to ordinary combustion, and is often called a supporter of combustion. Exclude air from a fire, and the fire goes out. When coal or wood burns, the carbon (of which they largely consist) unites with the oxygen of the air, forming thereby the invisible gas carbon dioxide, and the chemical change is manifested by heat and light. Chemically speaking, a substance burning in the air is uniting rapidly with oxygen. But since the air is about one fifth oxygen and four fifths nitrogen, — a gas which does not support combustion, — it follows that combustion is more vigorous in oxygen than in air.

The correct explanation of fire, burning, and combustion was first made by Lavoisier (1743-1794). For many years chemists had believed that all combustible substances contained a principle called **phlogiston**, and that when a substance burned, phlogiston escaped. Very combustible substances were thought to contain much phlogiston, and incombustible substances no phlogiston. This theory of combus-

tion was proposed by Becher (1635-1682) and advanced by Stahl (1660-1734). Many famous chemists—Priestley, Scheele, and Cavendish—supported it. Lavoisier, in 1775, proved by his own and others' experiments, that phlogiston did not exist, and that combustion is a process of combination with "a certain substance contained in the air." Soon after he identified this substance as oxygen. The theory of phlogiston, in spite of its falsity, exerted a wholesome influence on the development of chemistry.

Combustion, in a broad sense, is not necessarily oxidation, but chemical action which develops enough energy to produce light and heat. This broader meaning will be discussed later.

**Relation of Oxygen to Life.**—Oxygen is essential to all forms of animal and plant life. If an animal or a plant is deprived of air, it dies. By respiration air is drawn into the lungs and there it gives up part of its oxygen to the blood. This oxygen, which is distributed to all parts of the body by the blood, oxidizes the tissues of the body. As a result of this oxidation heat is supplied to the body and waste products are formed. One of these waste products is carbon dioxide gas, which with other gases is exhaled from the lungs. The blood during its circulation turns dark red, owing to the loss of oxygen; and when this dark red blood reaches the lungs, it receives a fresh supply of oxygen which turns it bright red, thus preparing it for another journey through the body. The food we eat contains carbon and other elements, which are built up into new tissue by complex chemical changes in the body. For simplicity we may think of the carbonaceous matter of the body as being slowly burned. The human body resembles a steam engine. In each, the oxygen of the air helps burn fuel largely composed of carbon. In the engine, the products escape through a chimney and the heat produced is used

to form steam which moves parts of the machine; in the body, the products escape mainly through the lungs and the heat keeps the body at a temperature at which it can best perform its functions.

It was formerly believed that breathing pure oxygen would produce too rapid oxidation in the body and burn up the tissue faster than it could be made. But recent study shows that with proper precautions oxygen may be breathed by a healthy person without producing any harmful effect. The blood apparently absorbs a maximum quantity of oxygen, whether supplied from air or from the pure gas. Oxygen is often administered to a person who has been suffocated, or to one who is unable to inhale enough air, as in cases of croup, asthma, or extreme weakness. It is sometimes used to sustain life where air is impure or rare, as in diving bells and submarine boats, and during balloon ascensions to a great height.

**Decay** is in part oxidation. The oxygen of the air together with water vapor acts upon animal and vegetable matter and slowly burns it up. The decomposition is often begun and hastened by bacteria. The products of decay are numerous, carbon dioxide being one. The oxygen dissolved by water assists in the decay of the impurities constantly flowing into rivers. Similarly, it oxidizes injurious vapors and matter in the air, literally burning them up, just as it burns wood in a stove. Hence, running water is more likely to be cleaner than standing or stagnant water, and the air in the open country or at the seashore purer than in the crowded city.

**Uses of Oxygen.**—Oxygen for commercial use is stored under pressure in strong iron cylinders. The pure gas has limited use, since air, although it contains about 80 per cent of the inert gas nitrogen, may usually be used in place of oxygen. A mixture of oxygen and hydrogen burned in a suitable apparatus produces an intensely hot flame, which is sometimes used to melt refractory metals and to produce the calcium light (see Oxyhydrogen Blowpipe).

**Liquid Oxygen.**—All gases at a low temperature (often exceedingly low) may be condensed to liquids, and even to solids. Under these conditions oxygen becomes first a pale blue liquid and finally a whitish solid. A small quantity was first obtained in 1877, but now it is prepared by the gallon. It is magnetic, and when a strong electromagnet is held near its surface, the liquid suddenly "leaps up to the poles and remains there permanently attached until it evaporates."

Under the normal pressure (760 mm.)<sup>1</sup> liquid oxygen boils at  $-182.5^{\circ}\text{C}.$ ; at this temperature its specific gravity is 1.130 (water = 1).

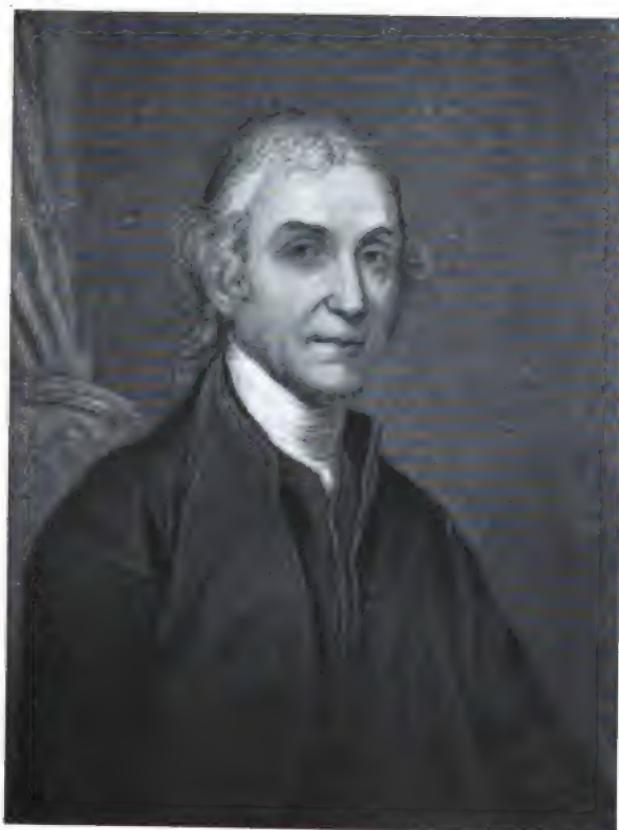
**Discovery of Oxygen.**—Oxygen was discovered on August 1, 1774, by Priestley (1733–1804). He prepared it by focusing the sun's rays upon the red mercury oxide by means of "a burning lens of twelve inches' focal distance." It was independently discovered by Scheele (1742–1786), a Swedish chemist, about the same time.

Priestley called the gas dephlogisticated air, because he regarded it as "devoid of phlogiston." Scheele called it empyreal air, *i.e.* fire air or fire-supporting air, because it assisted combustion. Lavoisier, in 1778, gave it the name *oxygen* (from the Greek *oxus*, acid, and *gen*, the root of a verb meaning to produce), because he believed from his experiments that oxygen was necessary for the production of acids—a view now known to be incorrect.

**Weight of a Liter of Oxygen.**—The volume occupied by a gas depends upon the pressure and temperature to which it is subjected. The volume increases with rise of temperature or with lowering of pressure, but decreases with fall of temperature or with increase of pressure. In general, if we cool a gas or subject it to a pressure, it shrinks, and if we heat a gas or decrease the pressure

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<sup>1</sup> This expression means the normal or standard pressure of the atmosphere as recorded by the barometer (see Chapter VI).



JOSEPH PRIESTLEY

1733-1804

THE DISCOVERER OF OXYGEN



it is under, it expands. Gas volumes, to be correctly compared, must therefore be at the same temperature and pressure. The normal or standard temperature is zero degrees on the centigrade thermometer, or briefly  $0^{\circ}$  C. The normal or standard pressure is the pressure of the atmosphere indicated by the barometer when the mercury is 760 millimeters high, or briefly 760 mm. Under these conditions, called standard conditions, a liter of dry oxygen weighs 1.429 gm. At another temperature or pressure the liter would contain a different quantity of oxygen and would therefore have a different weight. It is inconvenient to measure gases at  $0^{\circ}$  C. and 760 mm., so the observed volume is reduced to the volume it would occupy under standard conditions. This mathematical reduction is performed by applying the **Law of Charles** and the **Law of Boyle**.

**Law of Charles.** — It has been found by experiment that under constant pressure **all gases expand or contract equally for equal changes of temperature**. More explicitly, a gas expands or contracts  $\frac{1}{273}$  of its volume at  $0^{\circ}$  C. for every degree through which it is heated or cooled. This means that 273 volumes at  $0^{\circ}$  become 274 at  $1^{\circ}$ , 275 at  $2^{\circ}$ , 280 at  $7^{\circ}$ , 272 at  $-1^{\circ}$ , 270 at  $-3^{\circ}$ , or 273 +  $t$  volumes at  $t^{\circ}$  (*i.e.* at any temperature). This law is not absolutely correct, but its variations from the truth are slight.

Suppose we have 10 l. of oxygen at  $0^{\circ}$  C., and we wish to know the volume it would occupy at  $15^{\circ}$  C. The problem is easily solved by stating it as a proportion, thus —

$$273 : 273 + 15 :: 10 : x.$$

The value of  $x$  is the volume required. Conversely, in reducing 10 volumes at  $15^{\circ}$  C. to the volume occupied at  $0^{\circ}$  C., the proportion is —

$$273 + 15 : 273 :: 10 : x.$$

If the given temperature is below  $0^{\circ}$ , the number of degrees is subtracted from 273.

**Law of Boyle.** — It has also been found by experiment that under constant temperature **the volume of a gas is inversely proportional to**

**the pressure.** This is Boyle's law. It means that doubling the pressure halves the volume, and *vice versa*. Like the above law, this law is only approximately correct.

Suppose we have 10 l. of oxygen at 760 mm., and we wish to know the volume it would occupy at 775 mm. According to the law, the proportion expressing the relation is —

$$760 : 775 :: x : 10.$$

The value of  $x$  is the required volume. Conversely, if we have 10 l. at 775 mm., and wish to know its standard volume, the proportion is —

$$760 : 775 :: 10 : x.$$

It is convenient to notice that the proportion is stated so that the extremes (or means) are the original pressure and volume. In other words, one pressure multiplied by *its* volume equals the other pressure multiplied by *its* volume, or —

$$P : P' :: V : V'.$$

Hence, the proportion is applicable to values not necessarily including 760.

#### EXERCISES.

1. What is the symbol of oxygen ?
2. How is oxygen prepared (*a*) in the laboratory, and (*b*) commercially ?
3. Name several compounds from which oxygen can be prepared.
4. Summarize the properties of oxygen. What is its most characteristic property ?
5. If air contains something besides oxygen, what must be the general properties of this other ingredient ?
6. Define and illustrate (*a*) oxidation, (*b*) oxide, (*c*) combustion, (*d*) oxidizing agent.
7. What elements were mentioned in studying oxygen ? What compounds ?
8. What general chemical change is involved in burning ? What class of chemical changes is illustrated by (*a*) preparation of oxygen from mercuric oxide, (*b*) burning of sulphur in oxygen ?
9. Give a brief account of Priestley, Scheele, and Lavoisier (see Appendix, § 4).

10. What chemical part does oxygen take in (a) respiration, (b) decay, (c) combustion, (d) oxidation?
11. State and illustrate (a) Charles's law and (b) Boyle's law.
12. Give a brief account of Boyle and of Charles.

### PROBLEMS.

1. Potassium chlorate contains about 39 per cent of oxygen. How many grams of oxygen can be prepared from (a) 100 gm., (b) 250 gm., and (c) 725 gm. of potassium chlorate?
2. What approximate weight of oxygen can be prepared from 100 gm. of potassium chlorate containing 12 per cent of impurity?
3. What is the weight of (a) 10 l. of oxygen, (b) 75 l., (c) 500 cc., (d) 750 cc., (e) 4 l.?
4. A room 25 m. long, 17 wide, and 15 high is filled with oxygen. What weight of gas does it contain? (A liter of oxygen weighs 1.43 gm.)
5. Reduce the following volumes to the volume occupied at  $0^{\circ}\text{C}$ .: (a) 173 cc. at  $12^{\circ}\text{C}$ ., (b) 466 cc. at  $14^{\circ}\text{C}$ ., (c) 706 cc. at  $15^{\circ}\text{C}$ ., (d) 25 cc. at  $27^{\circ}\text{C}$ .
6. A volume of gas at  $0^{\circ}\text{C}$ . measures 1500 cc. What is its volume at (a)  $15^{\circ}\text{C}$ ., (b)  $50^{\circ}\text{C}$ ., (c)  $100^{\circ}\text{C}$ ., (d)  $300^{\circ}\text{C}$ .?
7. If 500 cc. of gas at  $27^{\circ}\text{C}$ . are cooled to  $-5^{\circ}\text{C}$ ., what is the new volume?
8. Reduce the following volumes to the volume occupied at 760 mm.: (a) 200 cc. at 740 mm., (b) 25 cc. at 780 mm., (c) 467 cc. at 756 mm.  
*Ans.* (a) 194.7, (b) 25.65, (c) 464.54.
9. A gas measures 1000 cc. at 770 mm. What is its volume at 530 mm.?
10. Reduce the following to standard conditions: (a) 147 cc. at 570 mm. and  $136.5^{\circ}\text{C}$ ., (b) 320 cc. at 950 mm. and  $91^{\circ}\text{C}$ ., (c) 480 cc. at 380 mm. and  $68.25^{\circ}\text{C}$ ., (d) 25 cc. at 780 mm. and  $27^{\circ}\text{C}$ ., (e) 14 cc. at 763 mm. and  $11^{\circ}\text{C}$ .

Ozone is a gas related to oxygen, though its properties differ. It is formed when electric sparks pass through the air, and is therefore produced when electrical machines are in operation and during thunder storms. Slow oxidation, especially of moist phosphorus, produces ozone. Indeed, its formation accompanies several chemical changes,

such as the burning of hydrogen and of certain resins, and the decomposition of water by electricity.

Ozone has a peculiar odor, suggesting burning sulphur. The name *ozone* signifies smell. It is active chemically, tarnishing metals, bleaching colored vegetable substances, deodorizing foul animal matter, and corroding such substances as cork and rubber. It is sometimes used as a disinfectant, though other oxidizing agents are more convenient. When heated to  $250^{\circ}\text{ C}.$ , or higher, it is wholly changed into oxygen. Ozone, therefore, contains nothing but oxygen. When oxygen is changed into ozone, it is found that three volumes of oxygen yield two volumes of ozone; and, conversely, the two volumes of ozone, when heated, become three volumes of oxygen. Hence, volume for volume, ozone is 1.5 times heavier than oxygen. For this reason ozone is sometimes called "concentrated oxygen," or "an oxide of oxygen." Its theoretical relation to oxygen will be subsequently discussed.

The atmosphere usually contains a small proportion of ozone, probably not more than one volume in 700,000 volumes of air. It is more abundant in the open country and at the seashore than in cities.

## CHAPTER III.

### HYDROGEN.

**Occurrence.**—Free hydrogen is present in the gases which escape from volcanoes, petroleum wells, and natural gas openings. Artificial illuminating gas contains considerable hydrogen. It is a product of fermentation and decay, and according to recent observations a very small quantity is present in the atmosphere of the earth. Enormous quantities of free hydrogen exist in the atmosphere of the sun, and during an eclipse of the sun gigantic streams of burning hydrogen may be seen shooting out from the sun's disk thousands of miles into space. Other heavenly bodies which are self-luminous, like the star Sirius and the nebulae, contain free hydrogen. The spectroscope has revealed its presence in these distant bodies. Meteorites, which come from regions far beyond our earth, often contain free hydrogen.

Combined hydrogen is abundant and widely distributed. It forms one ninth (by weight) of water. Most animal and vegetable matter contains hydrogen. It is also an essential component of all acids. Combined with carbon, it forms many gases and liquids called hydrocarbons, which are constituents of illuminating gas, kerosene, and naphtha. Combined with carbon and oxygen, it forms many vegetable compounds, such as sugar, starch, paper, wood, and numerous artificial products. With nitrogen it forms the familiar compound, ammonia; and with sulphur, the bad-smelling gas, hydrogen sulphide, which occurs in many sulphur springs.

**Preparation.**— Hydrogen, like oxygen, is prepared from its compounds. In the laboratory this is easily accomplished by allowing a metal and an acid to interact. The metals usually employed are zinc, iron, or magnesium, and the acids are dilute sulphuric acid or hydrochloric acid. The hydrogen comes from the acid and bubbles through the liquid, when the acid and metal are put into a test tube or flask. On a large scale hydrogen is prepared in a generator, which consists of a glass vessel provided with a delivery tube arranged to collect the gas over water in a pneumatic trough. No flame should be near during the performance of this experiment, because mixtures of air and hydrogen explode violently when ignited. The interaction of zinc and sulphuric acid produces, besides hydrogen, a compound called zinc sulphate. This remains in the generator in solution, and if the solution is allowed to evaporate, the zinc sulphate separates as transparent crystals, which soon turn white in the air. Hydrogen may be obtained from water by allowing the metal sodium and water to interact.

If a small piece of sodium is dropped upon cold water, the sodium melts into a shining globule, which spins about rapidly on the water with a hissing sound, and finally disappears with a slight explosion. But when the sodium is wrapped in a piece of tea lead pierced with a few holes and then dropped beneath the shelf of a pneumatic trough filled with water, the action proceeds smoothly. Hydrogen gas rises and displaces the water from a test tube or bottle supported over the hole in the shelf. The nature of the chemical change which attends the liberation of hydrogen from water will be explained later (Chapter V).

Hydrogen, together with oxygen, is liberated from water by passing a current of electricity through water containing a little sulphuric acid (see Chapter V).

Hydrogen may also be prepared by passing steam — the gaseous form of water — over heated metals.

This experiment was first performed by Lavoisier, in 1783, while he was studying the composition of water. He passed steam through a red-hot gun barrel containing bits of iron. The oxygen of the steam combined with the iron, and the hydrogen escaped from the tube. Since Lavoisier was studying the composition of water, and not the properties of hydrogen, he naturally thought of this gas as essential for forming water. So he says in his notes, "No name appears to us more suitable than that of hydrogen, that is to say, 'generative principle of water.'" Apart from historical interest, this experiment has commercial value. If steam is passed over red-hot coal (instead of iron), producer gas is formed. This is a mixture consisting largely of hydrogen, which is used as a source of heat in making steel and glass. If oil vapor is added to this mixture, water gas is formed. This is an illuminating gas like ordinary illuminating gas, and is used in many cities (see Water Gas).

**Physical Properties.** — Hydrogen has no taste or color. The pure gas has no odor, though hydrogen as ordinarily prepared has a disagreeable odor, due mainly to impurities in the metals used. Most of these impurities may be removed by passing the gas through a solution of potassium permanganate. Hydrogen is the lightest known substance. One liter of dry hydrogen at 0° C. and 760 mm. weighs only 0.0898 gm. Volume for volume, air is about 14.4 times, oxygen 16 times, and water 11,000 times heavier than hydrogen.

The extreme lightness of hydrogen may be easily shown. (1) If a wide-mouth bottle of the gas is left uncovered two or three minutes and a lighted match then dropped in, the match will continue to burn. If hydrogen had been present, the flame would have caused it to combine with the oxygen of the air with a loud explosion. (2) If a bottle of hydrogen is held beneath a bottle of air as shown in Figure 1, the gases



FIG. 1.—Pouring hydrogen.

soon exchange places, the hydrogen, owing to its lightness, rising into the upper bottle. Its presence there may be readily shown by dropping a lighted match into this bottle; if the experiment has been well done, the hydrogen will burn, but in most cases the loud explosion shows that only a part of the hydrogen has been poured upward. A lighted match dropped into the other bottle reveals only air. (3) If a small collodion, or rubber, balloon is filled with hydrogen and then released, it will rise rapidly into the air. Hydrogen, because of its lightness, is sometimes used to fill large balloons, but ordinary illuminating gas is usually employed.

Hydrogen is the standard for reckoning the density of gases. Thus, since a liter of oxygen weighs 1.43 gm., its density is found by the proportion:—  $0.0898 : 1.43 :: 1 : x$ .  $\therefore x = 16$  (nearly).

Hydrogen is not very soluble in water, but it is absorbed by several metals, especially the rare metal palladium. This property of absorbing gases is called **occlusion**.

Only about 1.84 l. of hydrogen at 760 mm. pressure dissolve in 100 l. of water at 20° C. Palladium absorbs from 370 to 960 times its own volume of hydrogen, according to the conditions of the experiment. Platinum and iron act similarly, though to a less degree. Illuminating gas, which contains considerable hydrogen, is also absorbed by metals. And since heat is developed by occlusion, the illuminating gas may be lighted by the heated metal upon which it flows. A self-lighting gas burner acts on this principle. The act of occlusion is partly chemical and partly physical.

Hydrogen illustrates **diffusion**; *i.e.*, it readily passes through porous substances and completely mixes with other gases without stirring or agitating.

It penetrates unglazed earthenware, paper, and heated metals, especially platinum. Hydrogen has the highest rate of diffusion, because its density is the lowest. The rate of diffusion of a gas is inversely proportional to the square root of the density. Thus, the rate of diffusion of hydrogen is four times that of oxygen, since the density of oxygen is sixteen times that of hydrogen. We are largely indebted for our knowledge of diffusion to the English chemist, Thomas Graham (1805-1869).

Hydrogen is not poisonous if pure. It does not support life, but a little may be breathed without danger.

**Chemical Conduct.** — Hydrogen burns in the air and in oxygen with an almost invisible but very hot flame. A platinum or copper wire held in the flame quickly becomes red-hot. If a small, dry, cold bottle is held over the flame, moisture is deposited inside the bottle. Water is the product of the combustion of hydrogen. These facts may be verified by the apparatus shown in Figure 2.

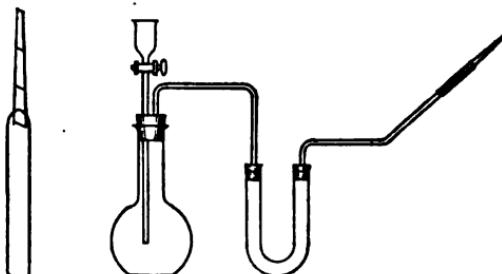


FIG. 2.—Apparatus for burning hydrogen. Acid is slowly introduced through the funnel into the flask, which contains zinc. The liberated hydrogen is dried as it passes through the U-tube containing calcium chloride and is lighted at the platinum tip after all the air has been driven from the apparatus. The tip, which is attached to the delivery tube by a small rubber tube, is shown (about actual size) on the left.

The film of water often noticed on the bottom of a vessel placed over a lighted gas range or a Bunsen burner is formed by the burning hydrogen and hydrogen compounds of the illuminating gas. Similarly, water often drops from the top of the oven of a lighted gas range. Organic substances containing hydrogen, such as wood and paper, when burned, yield water as one of their products.

The fact that the only product of burning hydrogen is water was first shown in 1783 by Cavendish (1730–1810). Lavoisier in the same year verified this fact and utilized it to explain the composition of water.

The temperature of the hydrogen flame is very high. More heat is produced by burning hydrogen in oxygen

than by burning the same weight of any other substance (see Chapter X).

Hydrogen burns in chlorine gas. The flame is bluish white, not very hot, and the product is hydrochloric acid gas—a compound of hydrogen and chlorine. This burning of hydrogen in chlorine illustrates the broader use of the word *combustion*, since no oxygen is involved.

Hydrogen does not support combustion, as the term is usually used. This fact is illustrated by putting a lighted taper into an inverted bottle of hydrogen. The taper ignites the hydrogen, which burns at the mouth of the bottle. The taper does not burn inside the bottle, but when it is slowly withdrawn through the burning hydrogen it is relighted. Hence, hydrogen burns, but does not support combustion.

A mixture of hydrogen and air explodes violently when ignited. Therefore, the air should be fully expelled from the apparatus in which hydrogen is being generated before the gas is collected, and no flames, large or small, should be near. Neglect of these precautions has caused serious accidents.

Hydrogen not only combines energetically with free oxygen, but it withdraws oxygen from compounds. As stated before, this chemical removal of oxygen is called **reduction**. Hydrogen is a vigorous reducing agent.

The **Oxyhydrogen Blowpipe** utilizes the intense heat produced by burning a mixture of hydrogen and oxygen. The



FIG. 3.—Oxyhydrogen blowpipe tip.  
and larger one for the hydrogen. Their pointed ends are

apparatus (Fig. 3) consists of two pointed metal tubes. The inner and smaller one is for the oxygen, and the outer

close together, and the two gases mix as they are forced out of these small openings by the pressure maintained in the storage tanks. Sometimes the tubes are separated, but the gases flow from a similar opening. The hydrogen is first turned on and lighted at the pointed opening; then the oxygen is turned on and the flow gradually regulated until the flame is the desired size, usually thin, straight, and as long as the apparatus requires. There is no danger in using the blowpipe, provided it does not leak and the pressure is properly regulated by the stopcocks. In the hot flame, some metals, like silver, turn to vapor; some, like iron, burn brilliantly; while others, like platinum, melt. When the flame strikes against a piece of lime or other substance difficult to melt, the lime becomes intensely bright. Thus used, it is called the **lime**, **calcium**, or **Drummond light** and is often employed in operating the stereopticon.

The **blast lamp** is a modification of the oxyhydrogen blowpipe. The apparatus (Fig. 4) consists of two tubes, an inner one for air and an outer one for illuminating gas. The air, which is forced through the apparatus by a bellows, provides oxygen, and the illuminating gas contains hydrogen and other combustible gases. The mixture burns at the opening of the tubes with a colorless or bluish flame, which is hotter than the Bunsen flame — the usual source of heat for chemical experiments. The shape of the flame is easily regulated by stopcocks.

**Liquid Hydrogen** is colorless and transparent. It was first obtained by Dewar in 1898. At the ordinary pressure of the atmosphere it boils at  $-252.5^{\circ}\text{C}$ . When cooled to about  $-256^{\circ}\text{C}$ . by evaporation under reduced pressure, the liquid becomes a mass of solid hydrogen; the latter is a white froth if produced while boiling, and a transparent solid if formed when quiet.

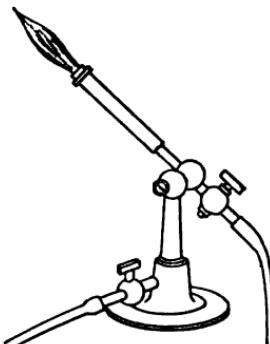


FIG. 4.—Blast lamp.

**Discovery of Hydrogen.**— Paracelsus in the sixteenth century obtained hydrogen by the interaction of acids and metals. It was identified as an element in 1766 by Cavendish, who called it inflammable air. The name *hydrogen*, given to it by Lavoisier, in 1783, is derived from the Greek words *hudor*, water, and *gen*, the root of a verb meaning to produce.

### EXERCISES.

1. What is the symbol of hydrogen?
2. What familiar compounds contain hydrogen?
3. How is hydrogen prepared in the laboratory? Describe other methods of preparation.
4. Summarize the properties of hydrogen. What is its most characteristic property?
5. Why is there danger of an explosion in generating hydrogen? How may the danger be avoided?
6. What is the weight of a liter of dry hydrogen? How many times heavier than a liter of hydrogen is one of air?
7. Define and illustrate (*a*) occlusion and (*b*) diffusion of gases.
8. What chemical change occurs when hydrogen burns in air?
9. Is water an oxide? Why?
10. How does the heat of the hydrogen flame compare with its luminosity?
11. Define (*a*) reduction and (*b*) reducing agent. Name a reducing agent.
12. Describe (*a*) the compound blowpipe and (*b*) the blast lamp, and state the use of each.
13. Summarize briefly the discovery of hydrogen. Give a short account of Cavendish. Why and by whom was hydrogen so named?
14. What class of chemical changes is illustrated by (*a*) the preparation of hydrogen from zinc and sulphuric acid, (*b*) the burning of hydrogen in air?

### PROBLEMS.

1. How many times heavier than a liter of hydrogen is a liter of oxygen, both being dry and under standard conditions?
2. What is the weight of (*a*) 500 cc. of dry hydrogen gas at 0° C. and 760 mm.? (*b*) Of 1800 cc.? (*c*) Of 9 l.?
3. The standard pressure at which a gas is measured is 760 mm. Express the same in inches.

## CHAPTER IV.

### GENERAL PROPERTIES OF WATER.

**WATER** is worthy of extensive study because of its importance in the animal, vegetable, and mineral kingdoms, its peculiar properties, and its numberless uses.

**Occurrence in Nature.**— Water, in the form of **vapor**, is always present in the atmosphere. Evaporation is constantly taking place from the surface of the ocean, from the moist earth, from the bodies of animals, and from plants. This vapor is continually condensing, and appears as clouds, mist, fog, rain, snow, hail, dew, and frost.

The proportion of water vapor in the atmosphere varies between wide limits, the amount present being largely influenced by the temperature. It has been found, however, that 1000 volumes of ordinary air contain about 14 volumes of water vapor. The total amount of vapor in the atmosphere is beyond comprehension.

In the **liquid state** water occurs in vast quantities. About three fourths of the surface of the globe is covered with water. Soil and porous rocks hold considerable quantities, and plants and animals contain a large proportion. Many substances which are apparently dry really contain a large proportion of water. Thus, in a ton of clover hay there are upwards of 200 lb. of water, and a ton of salt hay, which is usually very dry, contains about 100 lb.

Many common foods are largely water, as may be seen by the following —

TABLE OF THE PROPORTION OF WATER IN FOOD.

FOOD.	PER CENT OF WATER.	FOOD.	PER CENT OF WATER.
Cod . . . . .	82.6	Tomatoes . . . . .	94.3
Beef . . . . .	61.9	Apples . . . . .	84.6
Lobster . . . . .	79.2	Strawberries . . . . .	90.4
Eggs . . . . .	73.7	Watermelon . . . . .	92.4
Asparagus . . . . .	94.	Milk . . . . .	87.
Potatoes . . . . .	78.3	Cheese . . . . .	28 to 72
Cucumbers . . . . .	95.4	White bread . . . . .	35.3

The human body is nearly 70 per cent water, and during a year the average man drinks about half a ton.

Water in the form of ice permanently covers the coldest parts of the surface of the earth, *e.g.* the polar regions and the summits of high mountains. A rough estimate of the total weight of ice on the earth's surface is 6,373,000,000 millions of metric tons.<sup>1</sup>

**Functions of Water in Nature.**—Since water is the only liquid occurring in large quantities on the earth's surface, it is the great agent of **erosion**. It cuts away the earth's crust, and transports the material from higher to lower levels, or washes it into the ocean. Together with carbon dioxide gas it decomposes the rocks, changing them into clay, sand, and substances which make the soil productive. Its cycle of changes from liquid to vapor and vapor to liquid exerts a marked influence on the distribution of heat and moisture upon the earth's surface, *i.e.* on climate.

It dissolves many solids and gases and is constantly removing from the rocks and soil their soluble constituents,

<sup>1</sup> A metric ton contains 2204.6 pounds.

some of which serve for the nutrition of plants, though the larger part passes on to the ocean. The latter thus becomes a vast reservoir of water containing salt and other mineral matter obtained from the earth's crust. In the vital processes of animals and plants it helps change the food into a condition fit for distribution and assimilation.

**Industrial Applications.** — Besides the universal use of water for drinking, it is applied to an endless variety of useful and convenient purposes. It has always been man's beast of burden. It is the vehicle for transferring mechanical energy to water wheels—an application now being made on a vast scale for generating electricity. It utilizes by its peculiar properties the energy in fuel by means of the steam engine. It is the highway for transportation on the largest scale by ocean, river, lake, and canal. It is the vehicle for the distribution of heat by hot water and steam. It is the indispensable solvent in metallurgy, in the manufacture of chemicals, and in such industries as soap making, bleaching, brewing, dyeing, and tanning; it is necessary wherever mortar and cement are used. Man's work would be stopped in a thousand other ways were he deprived of water.

**Physical Properties of Pure Water.** — Owing to its remarkable solvent power, water is never found pure in nature, and is purified even in the laboratory only by taking especial precautions. At the ordinary temperature water is a tasteless and odorless liquid. It is usually colorless, but thick layers are bluish. Water is a poor conductor of heat.

This last property may be shown by boiling water near the surface in a large test tube containing a piece of ice weighted down upon the bottom. The ice remains unmelted for some time, although the water is boiling a few inches above it.

Most liquids expand with heat and contract with cold. Water is an exception. If water at  $100^{\circ}$  C. is gradually cooled, it contracts in volume. But when  $4^{\circ}$  C. is reached, if the cooling continues, the volume increases as long as the liquid state is maintained. Hence at  $4^{\circ}$  C. a given volume contains the greatest weight of water. That is, water has its **maximum density** at  $4^{\circ}$  C.

The density of water at  $4^{\circ}$  C. is 1; and water at this temperature is the standard for determining the densities of solids and liquids. Thus, when we say the density of gold is 19, we mean that gold is 19 times heavier than an equal volume of water at  $4^{\circ}$  C.

The expansion of water when cooled from  $4^{\circ}$  C. to  $0^{\circ}$  C. is slight, but the change is exceedingly important in nature. When the water on the surface of a lake or river cools, it contracts, and since it is heavier (volume for volume) than the warmer water beneath, it sinks. The warmer water rises, is cooled, and likewise sinks, thus causing a circulation which continues until all the water from surface to bottom has the temperature of  $4^{\circ}$  C. Now if the cooling continues, the surface water *expands* and remains on top, because it is lighter than the water beneath. Hence when the temperature of the air falls to  $0^{\circ}$  C., this top layer of water freezes and protects the remaining water from the cold, thus stopping the circulation. Should the circulation continue, as the temperature fell from  $4^{\circ}$  C. to  $0^{\circ}$  C., the whole body of water would finally freeze from top to bottom. This condition would not only destroy the fish and marine plants, but seriously affect climate, since the heat of summer could not melt such a vast mass of ice.

When water freezes, it expands about one tenth of its volume. That is, 100 cc. of water produce about 110 cc. of ice. In other words, 100 cc. of water and 110 cc. of ice weigh 100 gm. Hence ice floats. The specific gravity of ice is about 0.92.

The pressure exerted by water when it freezes is powerful. Vessels or pipes completely filled with water often burst when the water freezes. It is an erroneous but popular idea that "thawing out" a pipe bursts it. As a matter of fact, ice contracts when it melts. The pipe cracks when the water freezes, and as the ice melts a channel is left for the water to

flow out of the pipe. Because of this property, ice is an effective agent in splitting rocks. Water creeps into cracks, especially into the narrow ones by capillary attraction, and when it freezes, the rock is slowly split apart. Water in freezing also destroys the tissue of living plants, which are often said to have been "touched by frost." Frozen flesh for a similar reason becomes pulpy and is more liable to putrefy when thawed — a fact sometimes overlooked by those who eat flesh food which has been kept in cold storage.



FIG. 5.—Snow crystals.  
From photographs by Wilson A. Bentley.

Ice melts at  $0^{\circ}\text{C}.$  ( $32^{\circ}\text{ F.}$ ), which is also the freezing point of water. Ice often crystallizes in freezing, but the

individual crystals are seldom visible except during the first stages of the process. Snow crystals are common (Fig. 5). They are always six-sided, and are formed in the atmosphere by the freezing of water vapor.

Water evaporates at all temperatures, passing off as an invisible vapor into the atmosphere or into the air confined over it. If water is heated, the vapor passes off rapidly until the thermometer reads  $100^{\circ}\text{C}$ . (or  $212^{\circ}\text{F}$ .). At this point water boils, *i.e.* it changes rapidly into vapor without rise of temperature. This vapor, if allowed to escape into the atmosphere, cools and condenses quickly into a cloud of minute drops of water. This cloud is popularly called **steam**. Scientifically, steam is invisible. What we call steam is a mass of very small particles of water. This may be illustrated by boiling water in a large flask. The inside of the flask is perfectly transparent, although there is a cloud of "steam" issuing from its mouth.

Water boils when its vapor escapes with sufficient pressure to overcome the pressure of the atmosphere upon its surface. Hence the boiling point depends upon the pressure—either of the atmosphere or of the vapor within the vessel. The boiling point is  $100^{\circ}\text{C}$ . (or  $212^{\circ}\text{F}$ .) when the atmospheric pressure is normal, *i.e.* 760 mm. The boiling point is lower as the pressure is decreased and higher as the pressure is increased. Warm water will boil under the receiver of an air pump or on the top of a high mountain. In the city of Mexico (7500 feet above sea level) water boils at about  $92^{\circ}\text{C}$ ., and in Quito in South America (9350 feet above sea level) water, which boils at about  $90^{\circ}\text{C}$ ., is not hot enough to cook potatoes.

The pressure exerted by water vapor which escapes from a liquid is called **vapor pressure**. Since the rate of evaporation depends upon the temperature of the liquid, vapor pressure varies with the temperature. Vapor pressure is usually expressed in millimeters of mercury. Thus, at  $100^{\circ}\text{C}$ . the pressure of water vapor is 760 mm., because at the boiling point the vapor pressure is just enough to overcome the opposing atmospheric pressure. At  $20^{\circ}\text{C}$ . the pressure of water vapor is

17.39 millimeters. While at 0° C. the vapor pressure is only about 4.5 millimeters.

**Natural Waters.**—Water is never found pure in nature. Even rain water, which is usually regarded as the purest natural water, contains gases and dust washed from the air. When rain strikes the ground it begins at once to take up impurities from the rocks, soil, and vegetation. Some of the water flows along the surface, becoming more and more impure, and finally reaches the ocean. From 25 to 40 per cent of the annual rainfall in temperate regions soaks into the ground and trickles through the soil at an estimated rate of 0.2 to 20 feet a day. This underground water finally finds its way again to the surface as a spring or well, through a lake or river, or from a hillside. On its journey underground the water loses most, often all, of its organic matter,—remnants of vegetable and animal matter,—but dissolves mineral matter and gases. If the amount of dissolved matter in spring water is large or the kind of matter is so unusual as to give the water a marked taste or medicinal properties, the water is called **mineral water**. Water containing calcium and magnesium compounds is **hard**, but in **soft water**, such as rain water, these compounds are absent.

There are several hundred mineral springs in the United States. Those having a high temperature are called thermal, as at Hot Springs, Arkansas, and at Bath, England. Many contain a large proportion of common salt, as at Saratoga, New York. Others contain alkaline matter and carbon dioxide gas, *e.g.* Vichy and Apollinaris water. Sulphur springs contain solid or gaseous compounds of sulphur—or both—and have valuable medicinal properties. Some, like Hunyadi, are bitter; but others, especially those in New York State, which contain gaseous sulphur compounds, have a sweet taste but an unpleasant odor. Chalybeate waters contain soluble iron compounds. Many waters contain lime and magnesium compounds, and a few contain alum. Most natural

mineral waters contain traces of a large number of different substances. Many commercial mineral waters have doubtful medicinal value.

**River water** obviously contains the impurities brought by springs and the surface water; it is also often made very impure by decaying animal and vegetable matter, which has been purposely or accidentally introduced, especially if the river passes through a thickly settled region. A sluggish river is more apt to be impure than a swift one, because the latter tends to purify itself by exposing its impurities to the oxidizing power of the air. **Ocean water** contains a large proportion of common salt. The other substances in order of abundance are magnesium chloride, magnesium sulphate, calcium sulphate, and potassium sulphate; many other substances are present in small quantities. The peculiar taste of ocean water is due to the presence of these substances, and since by evaporation the water only is removed, the ocean always has a "salty" taste. The proportions of the solid substances in ocean water in their order of abundance are shown in the following:—

TABLE OF SOLID SUBSTANCES IN THE OCEAN.

SUBSTANCE.	PER CENT.	SUBSTANCE.	PER CENT.
Sodium Chloride . . .	77.76	Potassium Sulphate . . .	2.46
Magnesium Chloride . .	10.88	Calcium Carbonate . . .	.34
Magnesium Sulphate . .	4.74	Magnesium Bromide . . .	.22
Calcium Sulphate . . .	3.60	Other Substances . . .	traces

**Drinking Water.**—Water used as a beverage should of course be as pure as possible. As a rule the mineral matter in water selected for drinking is not injurious to

health; but since water may become contaminated with bacteria which produce diseases such as typhoid fever and cholera, it is usually necessary to purify the water before use.

The problem of obtaining suitable drinking water in large quantities is local. The water of many cities is purified by filtering it through a layer of sand and gravel, an acre or more in area and several feet deep. Such a filter removes bacteria almost completely, though it must be frequently cleaned. Sometimes the water is stored in a large settling basin or reservoir and purified by adding alum, or a similar substance, which causes the suspended matter to settle. Ozone is used as a purifier in some localities, and copper sulphate has been applied with varying results to stored water contaminated with certain kinds of organic matter. Dissolved substances cannot be removed without considerable difficulty, so as a rule water is taken from a source which is reasonably pure.

The purity of drinking water is usually determined by a **water analysis**. This is not a decomposition of water, but a chemical examination of a sample for the presence and amount of certain substances which indicate or cause impurity. A chemical examination is of limited value, however, unless it is supplemented by a microscopic study of a fresh sample and a rigid sanitary inspection of the premises. Water which is clear, sparkling, cool, attractive to the eye, and pleasant to the taste may be seriously polluted by disease germs, or may be liable to sudden contamination from some unsuspected source. On the other hand, a rather unpleasant-looking water may be harmless. Hence the necessity of careful and extended examination of water to be used as a beverage.

Water may be purified by **distillation**. This operation is not convenient with large quantities. It is performed in the laboratory in a condenser, which is shown in Figure 6 arranged for use.

The condenser consists of an outer tube, *AA*, provided with an inlet

and an outlet for a current of cold water, which surrounds the inner tube, *BB*. The vapor from the water boiling in the flask, *C*, condenses

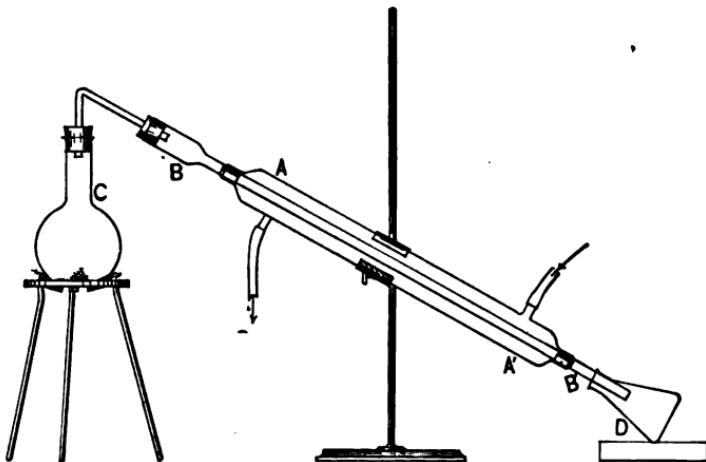


FIG. 6.—Condenser arranged for the distillation of water.

in the inner tube, owing to the decrease in temperature, and drops off at the lower end of this tube, as the **distillate**, into the receiver, *D*, while the impurities remain behind in the flask. Distilled water is prepared

on a large scale in metal vessels, and the vapor is condensed in a block tin pipe coiled around the inside of a vessel through which a current of cold water is flowing. This coiled pipe is called a **worm** (Fig. 7). Distilled water is used in the chemical laboratory; large quantities are made into ice. Distillation is an old process. A quaint still is shown in Figure 8. Distillation is the process used to separate liquids from solids and from each other,



FIG. 7.—Worm-shaped tube.

and finds extensive application in the manufacture of liquors and kerosene oil.



FIG. 8.—A quaint still.

**Solution.**—Many solids, liquids, and gases disappear when put into water. This operation is called dissolving, or putting into solution. The resulting liquid is called a **solution** of the substance used. The liquid in which the substance dissolves is called the **solvent**, and the dissolved substance is called the **solute**. If the solute is not volatile, or not very volatile, it may be recovered by evaporating, or distilling off, the water. The degree of solubility is usually expressed by the terms *slightly soluble*, *soluble*, and *very soluble*. It is more accurate, and usually desirable, to state the proportions of solvent and solute, and also the temperature. Thus, instead of saying that common salt is very soluble in cold water, it is better to state that 36 gm. of salt dissolve in 100 gm. of water at 20° C. Substances which do not dissolve in water are called **insoluble**, though this term is also applied to those substances a minute quantity of which dissolves in water. Thus glass, sand, and many rocks are usually classed as insoluble substances, but they dissolve appreciably in water.

A solution which contains a small proportion of solute is called a **dilute** solution ; one containing a large proportion is called a **concentrated** solution. Thus, dilute sulphuric acid usually contains one volume of acid to three or more volumes of water, while concentrated sulphuric acid is nearly 98 per cent acid. Sometimes the terms **weak** and **strong** replace dilute and concentrated, but they are ambiguous, and their use should be avoided.

**Solutions of Gases.**—Water dissolves or absorbs many gases. The degree of solubility depends upon the gas, the temperature of the water, and the pressure at which solution occurs. Some gases, such as ammonia and hydrochloric acid gas, are very soluble in water. Thus, one vol-

ume of water dissolves 1150 volumes of ammonia gas (at  $0^{\circ}\text{C}$ . and 760 mm.), 550 volumes of hydrochloric acid gas, and 80 volumes of sulphur dioxide gas, but only .02 of a volume of nitrogen gas.

The common gases, oxygen and hydrogen, are only slightly soluble in water. Air dissolves in water, as may easily be shown by heating faucet water, bubbles of air forming and escaping quickly as heat is applied. Carbon dioxide gas is quite soluble in water. Water containing this gas is called "soda water," or carbonated water. More gas is forced into the water than will dissolve at the ordinary temperature and pressure, as may be seen by the rapid escape of gas when the water is drawn from a soda fountain. This rapid escape of a gas is called **effervescence**. "Soda water" must, therefore, be stored in a strong vessel and kept in a cool place. The gas was formerly obtained from sodium bicarbonate — a compound related to "soda"; hence the name "soda water." It is now prepared from marble and an acid, or from liquid carbon dioxide.

The volume of gas which will dissolve in water decreases with rise of temperature. Thus, 100 cc. of water at  $0^{\circ}\text{C}$ . will dissolve 179.6 cc. of carbon dioxide, but only 90.1 cc. at  $20^{\circ}\text{C}$ . The volume of a moderately soluble gas which is dissolved by water is directly proportional to the pressure if the temperature is constant. This is **Henry's law**. It is illustrated by the following —

TABLE OF SOLUBILITY OF CARBON DIOXIDE GAS.

VOL. OF WATER AT $0^{\circ}\text{C}$ .	VOL. OF CARBON DIOXIDE MEASURED UNDER NORMAL CONDITIONS.	PRESSURE IN ATMOSPHERES.
1 l.	900 cc.	.5
	1800 cc.	1
	3600 cc.	2
	7200 cc.	4

The tremendous pressure to which subterranean gases are subjected accounts for their presence, especially carbon dioxide, in such large proportions in the waters of mineral springs.

**Solutions of Liquids.**—The solubility of liquids in water varies between wide limits. Some, such as alcohol and glycerine, are soluble in all proportions. Oils, such as kerosene, are practically insoluble; hence the old adage, "Oil and water will not mix." Carbon disulphide is almost insoluble, as may be seen by the formation, after agitation, of two distinct layers of liquid. The existence of two layers, however, is not always absolute proof of insolubility. Ether and water form two layers, but each dissolves appreciably in the other. In many cases a rise of temperature increases the solubility of liquids in water.

**Solutions of Solids.**—The solubility of solids in water is a matter of tremendous practical importance. The abundance of water and its power to dissolve such a vast number of different solids have led some to call water "the universal solvent." The far-reaching effect of this marvelous power in nature and its indispensable value to man have been considered. (See above.)

The degree of solubility of solids in water varies with the substance and with the temperature of the water. Some, like potassium permanganate, are very soluble, while others, like calcium sulphate, are difficultly soluble. In most cases solubility increases with a rise of temperature; hence the common practice of heating to hasten solution. The effect of increased temperature on solubility is sometimes very marked, the solubility being increased fourfold in some cases. Calcium hydroxide is less soluble in hot than in cold water, while common salt (sodium chloride) dissolves to about the same degree in each. There is a **limit to solubility**. That is, a given weight of water at a fixed temperature will dissolve a definite weight of solid and no more, although some undissolved solid remains in the water. The following table illustrates these properties.

TABLE OF SOLUBILITY OF SOLIDS IN WATER.

SOLIDS.	NUMBER OF GRAMS IN SOLUTION IN 100 GRAMS OF WATER.	
	80° C.	100° C.
Calcium chloride . . . . .	74	155
Copper sulphate (cryst.) . .	42.3	203.3
Magnesium sulphate . . . .	36.2	73.8
Potassium chlorate . . . . .	7.2	59.5
Potassium chloride . . . . .	35	57
Potassium dichromate . . . .	13	102
Potassium nitrate . . . . .	31.7	246
Potassium sulphate . . . . .	10.6	26
Sodium chloride . . . . .	36	39.7

A solution is **saturated** at a given temperature when it will dissolve no more solid, although undissolved solid is present. If a hot solution is cooled slowly, the solid soon begins to separate from the liquid, since solubility usually decreases with a fall of temperature. Often the solid is deposited in masses having a definite shape. This operation is called **crystallization**, and the masses are called **crystals** (see below). The shape and color of the crystal are characteristic of the substance, and serve to identify it. Thus, common salt crystallizes in cubes. Sometimes it is more convenient to evaporate a hot, concentrated solution. The point of saturation at the lower temperature is thus reached so gradually that the crystals can grow symmetrically. A brief account of crystals will be found in § 3 of the Appendix.

A solid can also be separated from a solution by **precipitation**. This may be done in two ways. (1) By adding a liquid in which the solid is not very soluble. Thus, when

water is added to an alcoholic solution of camphor, the liquid becomes turbid, because the camphor is almost insoluble in water. That is, the solid has been **precipitated** as very fine particles which remain suspended in the liquid for some time. Since the separated solid sooner or later falls to the bottom of the vessel, it is called a **precipitate**. (2) By changing the dissolved solid into another substance not soluble in the liquid. Such chemical changes are examples of **double decomposition**. Thus, when sodium chloride solution is added to silver nitrate solution a white, curdy precipitate of silver chloride is formed. A soluble silver compound has thus been changed into an insoluble silver compound, thereby removing the combined silver from the solution. So, also, a soluble chlorine compound (sodium chloride) has been changed into an insoluble chlorine compound (silver chloride), thereby removing the combined chlorine from the solution. Precipitation is a very common operation in chemistry.

Hot concentrated solutions of some solids, such as sodium sulphate and sodium thiosulphate, deposit no crystals, even when the solution cools. Such solutions are **supersaturated**. Supersaturation can occur only when the undissolved solid is not present. Hence, if a fragment of the solid is dropped into the supersaturated solution, crystals soon begin to form upon the fragment, and this separation continues until just enough solid is left in solution to produce saturation at the prevailing temperature. The amount of solid thus separated is often very great and sometimes forms a solid mass in the test tube. Saturation is analogous to stable equilibrium, while supersaturation resembles unstable equilibrium.

**Water of Crystallization.**—Crystals deposited from the water solution of many solids, even after they are dried,

contain water which is a part of the compound. This water is called **water of crystallization**. The crystals of some compounds, *e.g.* sodium carbonate and sodium sulphate, lose their water of crystallization and crumble on exposure to the air. This property is called **efflorescence**, and can be explained by the principle of vapor pressure. Substances containing water of crystallization exert vapor pressure. If this vapor pressure is greater than the pressure of the water vapor in the atmosphere, the substance loses water until the vapor pressures are equal or until all the water has escaped.

The proportion of water of crystallization in crystals is not arbitrary. It is constant in the same compound when crystallized under uniform conditions, but the proportion varies between wide limits in different substances. No explanation has been given of the varying amount of water of crystallization, nor of its necessity for the form and color of some crystals and not for others. Some well-crystallized substances contain no water of crystallization, *e.g.* potassium nitrate, potassium dichromate, sugar, and salt.

Crystals which have lost their water of crystallization by heat or exposure to air are said to be **dehydrated** or **anhydrous**. Thus, the grayish powder obtained by heating the blue crystallized copper sulphate is called dehydrated copper sulphate.

**Deliquescence.** — Many substances which are very soluble in water absorb water when exposed to the air, and become moist, or even dissolve in the water. Calcium chloride, sodium hydroxide, and potassium hydroxide belong to this class. This property is called **deliquescence**, and can be explained thus: Water vapor from the air condenses on the surface and produces a concentrated solution, which has a vapor pressure lower than the average pressure of the water vapor in the air. The solution continues to take up water until its vapor pressure equals the pressure of the water vapor in the air.

Common salt, or sodium chloride, often appears to deliquesce, especially in damp weather. The deliquescence is due, however, to the presence of magnesium and calcium chlorides. Sodium nitrate is somewhat deliquescent, and cannot be used in the manufacture of gunpowder, so potassium nitrate is used instead. This property of deliquescence is often utilized in the laboratory to remove water vapor from gases, calcium chloride being especially serviceable for this purpose.

**Thermal Phenomena of Solution.** — Solution is often accompanied by an appreciable change of temperature. When sulphuric acid is poured into water, heat is produced. With large quantities the heat is so great that the mixture often boils, and sometimes the hot acid is spattered. Hence, the acid should be added slowly to the water, and the mixture constantly stirred. Other substances which dissolve with the liberation of heat are fused calcium chloride, potassium hydroxide, and sodium hydroxide. Some which dissolve with a fall of temperature are crystallized calcium chloride, ammonium nitrate, ammonium chloride, and potassium nitrate. This subject is still under investigation.

**Solution and Chemical Action.** — Probably when a substance dissolves it is so modified that it can participate more readily in chemical changes. Hence, solution is an aid to chemical change, and is often an easy means of causing it. Thus, if dry tartaric acid and sodium bicarbonate are mixed, there is no evidence of chemical action; but when the mixture is poured into water, the copious evolution of carbon dioxide gas is conclusive evidence of a chemical change. Similarly, when a dry mixture of ferrous sulphate and potassium ferrocyanide is poured into water, the immediate appearance of a blue precipitate shows that the water was needed for the chemical change. Solution is such an important aid to chemical action that many substances employed in the laboratory are in solution, and many processes in chemistry are "wet" processes. Mention has already been made of the application of this fact to many industries.

**The Nature of Solution** has long been a subject of specu-

lation and study. The problem as a whole is still unsolved, though much light has been thrown upon the question by the behavior of solutions toward an electric current. According to prevailing views a solution which does not conduct electricity contains an unchanged solute, while a solution which does conduct electricity contains some unchanged solute together with particles into which some of the solute has dissociated (*i.e.* split up or decomposed). For example, a solution of sugar does not conduct electricity; hence this solution consists of the solvent (*i.e.* water) throughout which the undecomposed sugar is uniformly distributed. On the other hand, a solution of sodium chloride is an excellent conductor of electricity; therefore this solution consists of the solvent throughout which are distributed some undecomposed sodium chloride together with the two kinds of particles into which a portion of the sodium chloride has dissociated. The particles into which the solute dissociates are called ions. They are charged with electricity. Certain properties of solutions are ascribed to the nature and number of the ions in the solution. Thus, the sour taste of acids is attributed to hydrogen ions.

The detailed statement of the nature of solutions just given is a condensed form of the theory of electrolytic dissociation. This theory together with many underlying facts is fully discussed in later chapters. (See Chapters VIII and X.)

#### EXERCISES.

1. Mention several familiar properties of water.
2. In what forms does water exist?
3. Give the per cent of water in some familiar foods.
4. Develop the topics: '(a) water is an erosive agent; (b) water is a solvent in nature; (c) water has many industrial applications;

(d) water behaves exceptionally when heated from  $0^{\circ}\text{C}$ . to  $10^{\circ}\text{C}$ .;  
 (e) ice floats; (f) water is a cleansing agent.

5. Explain these expressions: (a) water has its maximum density at  $4^{\circ}\text{C}$ .; (b) the density of ice is 0.92; (c) steam is invisible; (d) the lower the pressure, the lower the boiling point; (e) 10 cc. per liter; (f) parts per million.

6. How do natural waters illustrate the solvent power of water?

7. What is (a) mineral water, (b) soft water, (c) hard water, (d) sulphur water, (e) chalybeate water?

8. What does ocean water contain? Why is the sea water salt?

9. What constitutes a safe drinking water? How may city water be purified? What is a water analysis?

10. Describe the operation of distillation. What is a condenser and why is it so named? Is distillation a new or an old process? Of what industrial use is it?

11. Define and illustrate (a) water of crystallization, (b) efflorescence, (c) deliquesce, (d) hygroscopic, (e) anhydrous, (f) dehydrated, (g) crystal, (h) crystallization.

12. Define and illustrate (a) solution, (b) solvent, (c) solute, (d) soluble, (e) slightly soluble, (f) very soluble, (g) insoluble, (h) dilute, (i) concentrated, (j) saturated solution, (k) supersaturated solution.

### PROBLEMS.

1. If 1.5 gm. of crystallized barium chloride lose 0.22 gm. when heated to constant weight, what per cent of water of crystallization does it contain?

2. If 2 gm. of another lot of barium chloride lose 0.295 gm., what per cent of it was water of crystallization?

3. If a liter of sea water has a density of 1.25, how many grams of "salt" does it contain?

4. If the density of ice is 0.92, what volume will a liter of water at  $4^{\circ}\text{C}$ . occupy when frozen? *Ans. 1.087 l.*

5. How much water (approximately) is contained in (a) 2 lb. of lobster, (b) 56 lb. of potatoes, (c) 1 lb. of tomatoes, (d) 2 lb. of milk, (e) 1 lb. of white bread, (f) a human body weighing 150 lb.?

6. If a kilogram of sea water contains 36.4 gm. of "salt," what per cent of the water is "salt"?

7. If a block of ice weighs 280 kg., what is its volume?

*Ans. 304.3 l.*

## CHAPTER V.

### COMPOSITION OF WATER.

**WATER** was considered an element until about the end of the eighteenth century. At that time it was shown to be a compound of hydrogen and oxygen. Many famous chemists worked on this problem.

The Composition of a Compound is determined either by analysis or synthesis, *i.e.* by taking it apart or putting its parts together. Sometimes both methods are used, since each method fortifies the other and strengthens the final conclusion. These methods find excellent application in determining the composition of water.

Analysis and synthesis may be qualitative or quantitative. A qualitative experiment is a study of the properties of elements and compounds with a view of discovering what they contain. A quantitative experiment is an accurate determination of the weight or volume of the components of a compound. Qualitative tests involve merely quality, while in quantitative tests quantity is the essential feature. Obviously, a complete determination of the composition of a compound requires both tests.

**Water contains Hydrogen.**—When steam is passed over heated metals, hydrogen is liberated. Lavoisier's demonstration of this fact has already been considered (see Preparation of Hydrogen). The fact that sodium liberates hydrogen from water at the ordinary temperature has also been discussed (see *ibid.*). If red litmus paper is put into the water from which the sodium has liberated hydrogen, the litmus paper becomes blue. This change

of color from red to blue shows that an alkali is in the water, because alkalies turn red litmus paper blue. The alkali is sodium hydroxide, and it may be obtained as a white solid by evaporating the water. Sodium hydroxide is a compound of sodium, hydrogen, and oxygen, and is formed by replacing part of the hydrogen of water by sodium. Since sodium liberates hydrogen from water, and forms at the same time a compound — sodium hydroxide — containing hydrogen, the hydrogen in water must be divisible into two parts. Now if 0.1 gm. of sodium is allowed to act upon water, 48.22 cc. of hydrogen are liberated; and if the sodium hydroxide thus formed is dried and heated with sodium, 48.22 cc. more of hydrogen are obtained. This shows that the hydrogen in water is divisible into two *equal* parts — a fact which will soon be utilized.

**Water contains Oxygen.** — The fact that oxygen is a component of water has already been suggested, *e.g.* (1) by the production of water when hydrogen is burned in air, (2) by the formation of a compound of iron and oxygen when steam is passed over hot iron, and (3) by the formation of sodium hydroxide when sodium acts upon water. These proofs, however, are all indirect. A simple direct demonstration of the presence of oxygen in water may be made by allowing chlorine water to stand in the sunlight. (Chlorine water is prepared by saturating water with chlorine gas — an element to be studied in Chapter XI.) A long tube like that shown in Figure 9 is completely filled with chlorine water, the open end is immersed in a vessel containing some of the same solution, and the whole apparatus is placed in the direct sunlight. Bubbles of gas soon appear in the liquid, and after a few hours a small volume of

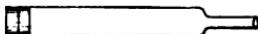


FIG. 9. — Tube for decomposition of water by chlorine.

gas collects at the top of the tube. This gas may be shown, by the usual tests, to be oxygen.

**The Electrolysis of Water** is its decomposition by electricity. It is accomplished in the apparatus shown in



FIG. 10.—Hofmann apparatus for electrolysis of water.

Figure 10. Since pure water does not conduct electricity, sulphuric acid is added. Enough of this acid mixture is poured into the apparatus to fill the reservoir half full after the stopcocks have been closed. As soon as an electric battery of two or more cells is connected by wires with the piece of platinum near the bottom of each tube, bubbles of gas form on the platinum, and as the action proceeds, the bubbles rise and displace the water in each tube. The volume of gas is greater in one tube. Assuming that the tubes have the same diameter, the volumes are in the same ratio as their heights, which will be found by measurement to be two to one. The larger volume of gas is hydrogen and the smaller one is oxygen. Many accurate repetitions of this experiment have shown that only hydrogen and oxygen are produced, and that the ratio of their volumes is two to one. It has also been shown that the sum of the weights of the two gases equals the weight of the water decomposed. The whole experiment demonstrates that

water is a compound consisting of two volumes of hydrogen combined with one volume of oxygen.

Water was first decomposed by electricity in 1800 by Nicholson and Carlisle. Davy confirmed their work by a series of brilliant experiments extending through a period of six years (1800-1806). During this time he not only proved that the volume of hydrogen is double that of oxygen, but by electrolyzing water in a gold vessel placed in an atmosphere of hydrogen, he proved that nothing but these gases is produced.

**The Quantitative Composition of Water.**—The foregoing facts about the composition of water have been mainly qualitative. They have shown by analysis and synthesis that water consists of hydrogen and oxygen, and that the ratio of their volumes is approximately two to one. Decisive evidence of the quantitative composition of water is obtained by a determination of its volumetric and its gravimetric composition. Volumetric means "by volume" and gravimetric means "by weight."

**The Volumetric Composition of Water** is determined by exploding a mixture of known volumes of hydrogen and oxygen in a eudiometer.

Gas volumes which are to be compared with each other must be dry and at the same temperature and pressure. This requirement, which is called the "standard condition," is inconvenient, and almost impracticable. Hence, it is customary to measure each volume of moist gas under the existing conditions, and then reduce the observed volume to that volume which the gas would occupy if standard conditions prevailed. The reduction to standard conditions is accomplished by the formula —

$$V = \frac{V' (P' - a)}{760(1 + .00366 t)}.$$

In the formula<sup>1</sup> —  $V$  = the corrected volume.

$V'$  = the observed volume.

<sup>1</sup> A complete discussion of the laws of gases, the principles which control their measurement, together with the development of the above formula for reduction to standard conditions, may be found in Appendix B of the author's "Experimental Chemistry." See also the Laws of Boyle and Charles in Chapter II, and Vapor Density in Chapter IV (this book).

$P'$  = the observed pressure.

$t$  = the observed temperature.

$\alpha$  = the vapor tension at  $t^{\circ}$  C.

A convenient form of apparatus for determining the volumetric composition of water is shown in Figure 11. The essential part is the eudiometer,  $F$ . In this graduated glass tube the gases are accurately measured and exploded. The electric spark which causes the explosion is

obtained from an induction coil and battery. The spark leaps across the space between the platinum wires at the top of the eudiometer, and the heat produced by this spark causes the hydrogen and oxygen to combine and form water. Oxygen and hydrogen are introduced separately into the eudiometer, measured, and exploded. After the explosion, which is indicated by a slight click

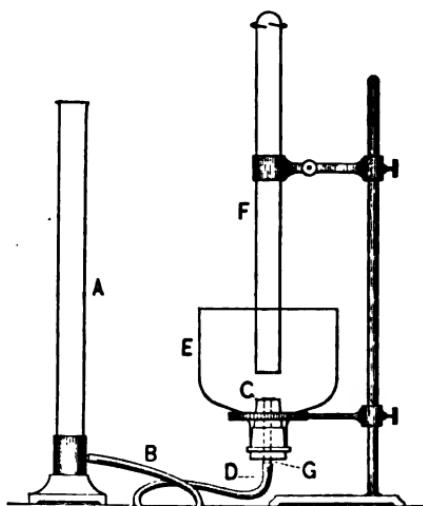


FIG. 11.—Apparatus for determining the volumetric composition of water.

or flash of light, water from the reservoir,  $E$ , rushes up into the eudiometer. The water does not completely fill the tube, because an excess of one gas is added. This additional gas takes no part in the chemical change, but merely serves to lessen the violence of the explosion, which otherwise might break the eudiometer. The quantity of water formed by the union of the hydrogen and oxygen

is too minute to measure. The most accurate experiments give the ratio 2.0027 to 1, but as usually stated the volumetric composition of water is 2 volumes of hydrogen and 1 volume of oxygen.

The discovery of the volumetric composition of water was not made by one chemist alone. Priestley, about 1780, noticed that when a mixture of air and hydrogen was exploded, "the inside of the glass, though clear and dry before, immediately became dewy." Cavendish, in 1781, showed that when a mixture of two parts hydrogen and one part oxygen was exploded, nothing but water was formed. Watt, in 1783, was the first to state that water is a compound, though he performed no experiments and probably did not understand the real nature of its components. Lavoisier in the same year verified many facts previously noticed but not completely understood, and undoubtedly first clearly recognized and stated what his contemporaries had overlooked. The final proof of the volumetric composition of water was an accurate verification in 1805 by Gay-Lussac and Humboldt of the previous observation that two volumes of hydrogen unite with one volume of oxygen.

**The Gravimetric Composition of Water** is determined by passing dry hydrogen over copper oxide. The method depends upon the fact that many oxides, such as those of lead, copper, and iron, when heated in a current of hydro-

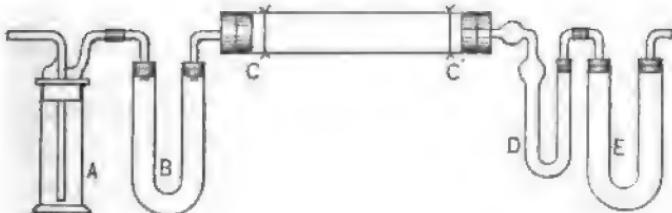


FIG. 12.—Apparatus for determining the gravimetric composition of water.

gen, give up their oxygen, or, chemically speaking, these oxides are reduced to metals. By this reduction the oxygen of the oxide combines with the hydrogen, thereby forming water which is collected in a weighed tube.

A convenient form of apparatus is shown in Figure 12. The copper oxide is placed in the combustion tube, *CC*, which is made of hard glass. The Marchand tube, *D*, which is filled with calcium chloride, collects and retains the water formed in the combustion tube, as the hydrogen passes over the hot copper oxide. The tubes *A*, *B*, and *E* keep moisture out of the apparatus. The experiment is very simple. Copper oxide is placed in the combustion tube, which is then carefully weighed. The Marchand tube, being filled with calcium chloride, is also weighed. After the other tubes are properly filled and the hydrogen generator adjusted, the tubes are connected as shown in the figure. The combustion tube is now heated, and moisture collects in it; as the heat increases the copper oxide glows, and the moisture passes into the Marchand tube. When the operation is over and the apparatus is cool and free from hydrogen, the combustion tube and Marchand tube are weighed. The gain in weight of the Marchand tube is the weight of the water formed, while the loss in weight of the combustion tube is the weight of the oxygen contained in this water. An illustration will make this clear. Dumas and Stas, who performed this experiment accurately in 1843, found substantially that the combustion tube lost 5.251 gm. of oxygen, while the Marchand tube gained 5.909 gm. of water. Now the 5.251 gm. of oxygen united with 0.658 gm. of hydrogen (*i.e.*  $5.909 - 5.251 = 0.658$ ). But 0.658 and 5.251 are in the same ratio as 1 and 7.98. This ratio is very nearly 1 to 8, and the gravimetric composition of water is often stated as 1 part hydrogen and 8 parts oxygen. Occasionally the gravimetric composition is stated in per cent, the values being 11.18 per cent hydrogen and 88.82 per cent oxygen; sometimes it is stated as 2 parts hydrogen to 16 parts oxygen.

The ratio obtained by Dumas was scarcely questioned until a few years ago. It now appears from an exceptionally accurate determination by Morley that the ratio is 1 to 7.9395. He effected a complete synthesis of water in which the oxygen, hydrogen, and water were weighed. This ratio is now accepted as the correct one.

The gravimetric composition of water was first determined about 1820 by Berzelius and Dulong. Their work was verified by Dumas and Stas in 1843. Morley's synthesis was made in 1895.

A Comparison of the Volumetric and Gravimetric Composition of Water shows that the results of the two methods agree. One volume of oxygen is sixteen times heavier than an equal volume of hydrogen (see Density of Hydrogen). Therefore, the one volume of oxygen must be eight times heavier than the two volumes of hydrogen in water. That is, the oxygen in water weighs eight times more than the hydrogen. But this is the ratio actually found in determining the gravimetric composition of water by an independent experiment. These facts strengthen our belief that the composition of water is approximately —

By weight, one part hydrogen and eight parts oxygen.

By volume, two parts hydrogen and one part oxygen.

**Summary.** — The following facts have been shown concerning the composition of water : —

- (1) Water is a chemical compound of hydrogen and oxygen.
- (2) It is formed when hydrogen is burned in air, or when a mixture of hydrogen and oxygen is exploded.
- (3) It can be decomposed by electricity into hydrogen and oxygen in the ratio of two volumes of hydrogen to one volume of oxygen.

(4) Sodium liberates hydrogen from water and forms at the same time a solid containing a quantity of hydrogen equal to the quantity of hydrogen liberated. Iron, other metals, and carbon liberate hydrogen from water, forming at the same time an oxide of the respective substance.

(5) Chlorine liberates oxygen from water.

(6) Two volumes of hydrogen, when exploded with one volume of oxygen, combine to form water, and the weight of the water formed equals the weight of the gases used.

(7) Water is formed by the union of two parts by weight of hydrogen and sixteen parts by weight of oxygen.

#### **EXERCISES.**

1. How is the composition of a compound determined ?
2. Define (*a*) synthesis, (*b*) analysis, (*c*) qualitative, (*d*) quantitative, (*e*) volumetric, (*f*) gravimetric.
3. How would you prove that water is composed of hydrogen and oxygen ?
4. How do we know that the hydrogen in water is divisible into two equal parts ?
5. What is the electrolysis of water ? How is it accomplished ? What does it prove about the composition of water ? When and by whom was it first performed ? What did Davy contribute toward the solution of the problem ?
6. What is the volumetric composition of water ? How is it determined ? Who worked on this problem, and what did each contribute to its solution ?
7. Answer the same questions (as in 6) about the gravimetric composition of water.
8. Compare the volumetric and the gravimetric composition of water.
9. What does the burning of hydrogen show about the composition of water ?
10. Summarize the essential facts regarding the composition of water.

11. Give a brief biographical account of (*a*) Nicholson and Carlisle, (*b*) Dumas, (*c*) Humboldt, (*d*) Stas, (*e*) Watt, (*f*) Gay-Lussac (see Appendix, § 4).

### PROBLEMS.

1. What weight of (*a*) hydrogen and (*b*) oxygen can be obtained by decomposing 125 gm. of water?
2. What volume of (*a*) hydrogen and (*b*) oxygen can be obtained by decomposing 9 l. of water?
3. What weight of hydrogen must unite with 16 gm. of oxygen to form water? What weight with (*a*) 40 gm., (*b*) 70 gm., (*c*) 160 gm.?
4. What volume of oxygen must unite with 2 l. of hydrogen to form water? What volume with (*a*) 40 l., (*b*) 40 cc., (*c*) 40 qt., (*d*) 95 volumes, (*e*) 160 l.?
5. What volume of oxygen is necessary to unite with 100 gm. of hydrogen to form water? (Suggestion: What is the weight of a liter of oxygen?)
6. Hydrogen is passed over 2.48 gm. of hot copper oxide, which at the end of the experiment weighed 2.24 gm.; the water formed weighed 0.27 gm. In what ratio did the hydrogen and oxygen combine?
7. Berzelius and Dulong, in 1820, obtained the following results in their determinations of the gravimetric composition of water: Loss of weight of copper oxide (in grams), 10.832 and 8.246. Weight of water formed, 12.197 and 9.27. Calculate in each case the ratio in which the hydrogen and oxygen combined. What is the average ratio?
8. Dumas and Stas repeated the above work in 1843, and found as an average of nineteen determinations, that 840.161 gm. of oxygen formed 945.439 gm. of water. Calculate the ratio of combination.

**Hydrogen Dioxide** is a liquid composed of hydrogen and oxygen. But the proportion of the components is not the same as in water. It contains *two* parts of hydrogen and *thirty-two* parts of oxygen by weight. It is often called, especially in commerce, **hydrogen peroxide**, because its relative proportion of oxygen is greater than in water — the other hydrogen oxide.

It is manufactured by treating barium dioxide (or peroxide) with sulphuric or hydrochloric acid. The commercial solution has a variable strength, and usually contains three or more per cent of hydrogen dioxide. It has a sharp, pungent odor, and a bitter, metallic taste.

Hydrogen dioxide is an unstable compound; it decomposes slowly at the ordinary temperature, and very rapidly if heated. The dilute, commercial solution is somewhat stable, but heat decomposes it completely into water and oxygen. The ease with which it yields oxygen makes it a good oxidizing agent. In this respect, hydrogen dioxide resembles ozone, and, indeed, they are sometimes mistaken for each other. It is also a reducing agent, and is frequently used as such in the laboratory. It is used extensively to bleach animal and vegetable matter, such as human hair, ostrich feathers, fur, silk, wool, cotton, bone, and ivory. It is also used as an antiseptic and disinfectant in surgery. Large quantities are used to restore the color to faded paintings — a use suggested by Thénard, the discoverer. In the laboratory it is proving a serviceable reagent.

Hydrogen dioxide is found in the air, in rain and snow, but the proportion is variable and exceedingly small.

## CHAPTER VI.

### THE ATMOSPHERE—NITROGEN.

The **Atmosphere** is the great mass of gas surrounding the earth and extending into space. Its estimated height is fifty to several hundred miles. We live at the bottom of this vast ocean of *air*, as it is often called.

Aristotle (384-322 B.C.) regarded air as one of the four elementary principles whose combinations made up all substances in the universe. The other three were earth, fire, and water. He taught that air possesses two fundamental properties,—heat and dampness. The early chemists used the word *air* in the sense in which the word *gas* is now employed. Thus, we have already learned that hydrogen was first called inflammable air.

The terms *atmosphere* and *air* are often used interchangeably, though by air we usually mean a limited portion of the atmosphere. Many skillful chemists have studied the action of air on living things, its relation to combustion, the effect of its weight, its composition, and its varied properties. Their work has contributed many fundamental facts to science.

**General Properties of the Atmosphere.** — Air has weight. We often use the expression “light as air.” But a cubic foot of air weighs 1.28 oz. and a room  $40 \times 50 \times 25$  ft. contains about two tons of air. The total weight of the atmosphere has been estimated to be five thousand millions of millions of tons. This enormous mass resting upon the earth exerts a pressure which is about fifteen pounds on every square inch. This amount of pressure upon a

square inch is called "an atmosphere," and it is sometimes used as a unit of pressure. Thus, three atmospheres means a pressure of forty-five pounds per square inch. It is this pressure which causes water to rise in pumps and flow through siphons. Atmospheric pressure is exerted in all directions and is variable. It is measured by the barometer. The normal or standard pressure of the atmosphere is equal to the weight of a column of mercury one square inch in cross section and 29.92 in. high, or one square centimeter in cross section and 760 mm. high. But since atmospheric pressure is at the rate of fifteen pounds to the square inch, it is necessary to know the height only of the mercury column in order to know the pressure.

The pressure of the atmosphere varies as the height and the composition of the atmosphere vary, and the barometer changes accordingly. The weight of a liter of dry air at  $0^{\circ}$  and 760 mm. is 1.293 gm.

The appreciable movements of the atmosphere are the winds.

**Ingredients of the Atmosphere.** — The atmosphere is a mixture of several gases. But since this mixture always contains about 78 parts of nitrogen and 21 parts of oxygen by volume, we often speak of air as consisting solely of these two gases. Besides this large proportion of oxygen and nitrogen, the air always contains small and variable proportions of water vapor and carbon dioxide gas. Besides these four ingredients, air always contains the gases argon and helium, and usually ozone, hydrogen, hydrogen peroxide, compounds related to ammonia and nitric acid, dust, and germs. The composition varies but slightly in different localities. Near the city air may contain a relatively larger proportion of dust, ammonia, sulphur compounds, and acids; in the country the proportion of ozone is relatively large; at the ocean the air contains considerable salt.

**General Properties of Nitrogen.** — The chemical element, nitrogen, constitutes about 78 per cent of the atmosphere (by volume). It is a colorless gas, and has no taste or odor. It is somewhat lighter than air, and is very slightly soluble in water. In many respects it differs markedly from oxygen. Thus it will not support combustion, neither will it burn nor sustain life. Animals die if left in nitrogen.

The fact that a candle flame quickly goes out and a mouse soon dies in nitrogen was first observed by Rutherford, an English physician, who discovered the gas in 1772. Soon after, Lavoisier showed the true relation of nitrogen to the atmosphere. To emphasize the inability of the gas to support life, he called the new gas *asote*, the name now used for it by some French chemists.

Nitrogen is not poisonous, for a large proportion of the air we breathe is nitrogen. Its function in the atmosphere is to dilute the oxygen. It is an inert element. It combines with only a few other elements, and many of its compounds easily decompose.

**Oxygen and Nitrogen in the Atmosphere.** — The chemical activity of the atmosphere is due to the free oxygen it contains. We have already learned that oxygen is an active chemical element. If the air were largely oxygen, rusting and decay would proceed with astounding rapidity, and fires once started would burn with great violence. On the other hand, nitrogen is inactive. And if the air contained much more than the normal amount, chemical action would be slower. Oxygen alone is too active, while nitrogen alone is inactive. To be serviceable to man, oxygen must be diluted with nitrogen, while nitrogen must be accompanied by a small proportion of oxygen.

The presence of oxygen and nitrogen in the atmosphere, and the functions of the two gases, were first clearly explained by Lavoisier in 1777, though many others — Boyle, Priestley, Rutherford, and Scheele — helped solve the problem.

**Composition of the Atmosphere.** — Samples of air from various parts of the globe show a remarkable uniformity of composition. Until 1895 it was supposed that pure air consisted solely of oxygen and nitrogen. But it has been found that about two per cent of the gas hitherto called nitrogen is argon, a gas so much like nitrogen, and so difficult to separate from the latter, that for years it had been overlooked (see Argon, below). According to the most recent results, the following is —

#### THE COMPOSITION OF PURE DRY AIR.

INGREDIENT.	PERCENTAGE.	
	By volume.	By weight.
Nitrogen . . . . .	78.122	75.539
Oxygen . . . . .	20.941	23.024
Argon . . . . .	0.937	1.437

The composition of the atmosphere was studied by Priestley, but his results were conflicting. Cavendish, in 1781, was the first to show that the proportion of oxygen and nitrogen in air is nearly constant. Since his time this result has been confirmed by many chemists, especially by Bunsen, who is widely known as the inventor of the Bunsen burner, which is used as a source of heat in chemical laboratories.

**The Volumetric Composition of the Air** may be found by introducing a known volume of pure air into a eudiometer and exploding it with a known volume of hydrogen. The oxygen of the air combines with twice its volume of hydrogen, forming a minute quantity of water; hence one

third of the diminution in volume is the volume of oxygen in the air. The difference between the volume of oxygen found and the original volume of air is the volume of nitrogen and argon.

An illustration will make this experiment clear. Suppose (1) we mix and explode 100 cc. of air and 50 cc. of hydrogen, or 150 cc. in all, and (2) that the residue measures 87 cc. Now,  $150 - 87 = 63$ , hence 63 cc. of the total volume combined to form water. But one third of 63 cc. is oxygen, which came from the original volume of air. Hence,  $63 + 3 = 21$ , the volume of oxygen in 100 cc. of air. The remainder, 79 cc., is nitrogen and argon.

**Another Method**, often used to determine the volumetric composition of the air, is based on the fact that phosphorus will combine slowly with oxygen, even at the ordinary temperature. The operation is performed in an apparatus like that shown in Figure 13. A piece of phosphorus, C, attached to a wire, is inserted into a graduated glass tube, B, containing a measured volume of air. White fumes indicate immediate action. These fumes are solid particles of an oxide of phosphorus called phosphorus pentoxide. They soon dissolve in the water, which rises higher in the tube, as the oxygen combines with the phosphorus. In a few hours the phosphorus is removed, and the volume of gas is read. The difference between the first and last volumes is oxygen. The gas remaining in the tube is, of course, a mixture of nitrogen and argon. In performing this experiment unusual care must be taken not to touch the phosphorus with the dry hands.

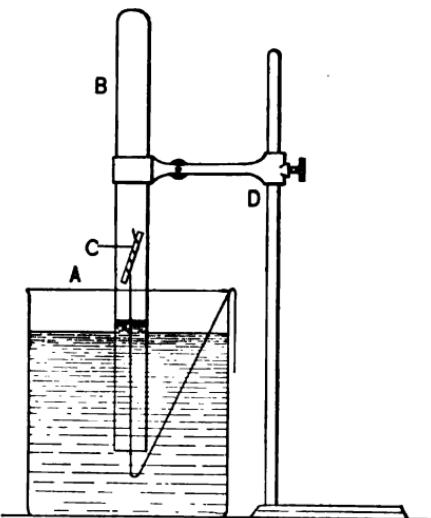


FIG. 13.—Apparatus for determining the composition of air by phosphorus.

The Gravimetric Composition of Air was first accurately determined in 1841 by the French chemists, Dumas and Boussingault. The average result of many experiments was—

Oxygen . . . . 23 parts by weight.

Nitrogen . . . . 77 parts by weight.

We know, however, that the correct proportions are—

Oxygen . . . . 23.024 parts by weight.

Nitrogen . . . . 75.539 parts by weight.

Argon . . . . 1.437 parts by weight.

They passed pure air through a weighed tube containing copper, and arranged so that heat could be applied. The oxygen of the air combined with the copper, while the nitrogen passed on into a weighed globe. Both tube and globe increased in weight. The increase in the tube was the weight of the oxygen, while the increase in the globe was the weight of the nitrogen.

**Water Vapor in the Atmosphere.**—Water vapor is always present in the atmosphere, owing to the constant evaporation from the ocean and other bodies of water. The total amount present is large, though variable. A given volume of air will absorb a definite volume of water vapor and no more, and the amount depends largely upon the temperature. Air containing its maximum amount of water vapor is said to be saturated at that temperature, or to contain 100 per cent of water vapor. The saturation point is also called the **dew point**. On a pleasant day the **relative humidity**, *i.e.* the relative amount of water vapor present, may vary from 30 to 90 per cent, the average being about 50 per cent. Warm air holds more vapor than cool air. The amount of water vapor in the air has a marked influence on the physical condition of man. The depressing weather during "dog days" is due to the

high relative humidity of the air, which sometimes reaches 95 per cent. The absence of life in deserts is largely due to the dry air above them. Much of the languor felt in a "close" room or crowded hall is partly caused by the excess of water vapor in the "bad" air. The presence of water vapor in the air is shown by the moisture which collects on the outside of a vessel containing cold water, such as a pitcher of iced water. The moisture comes from the air around the vessel. For a similar reason, water pipes in a cellar and the cellar walls themselves are moist in summer. The deliquescence of calcium chloride, common salt, and other substances likewise reveals the presence of water vapor in the air (see Deliquescence).

When the temperature of the air falls, the water vapor condenses and is deposited in the form of dew, rain, fog, mist, frost, snow, sleet, or hail. The clouds are masses of water vapor which has been condensed by the cold upper air.

**Carbon Dioxide in the Atmosphere.**—Carbon dioxide is one product of the respiration of animals, and of the combustion and decay of organic substances. By these processes an immense quantity of carbon dioxide is being constantly poured into the atmosphere. The quantity in the atmosphere is variable, though not between such wide limits as the water vapor. The proportion in normal air is about 4 parts in 10,000 parts of air. Over the ocean the proportion is smaller, but in the air of cities it is greater. In crowded rooms the proportion is often as high as 33 parts in 10,000, because carbon dioxide is exhaled faster than it can be removed. The proportion of carbon dioxide in the atmosphere as a whole is practically constant, largely owing to the fact that this gas is an essential food of plants (see Carbon Dioxide). The presence of carbon dioxide in the air is detected by limewater.

If limewater is exposed to the air, the carbon dioxide unites with the lime in the limewater, forming a thin, white crust of insoluble calcium carbonate on the surface of the limewater. If air is drawn through lime-water, the liquid becomes milky, because the particles of calcium carbonate are suspended in the liquid. The purity of air is often determined by finding out what proportion of carbon dioxide it contains. If a known volume of dry air is drawn through a known weight of limewater or similar liquid, the increase in weight will be the weight of carbon dioxide in the volume of air used.

The different gases in the atmosphere are not arranged in layers according to their densities. They are in constant circulation (see Diffusion). Hence carbon dioxide, though heavier than oxygen and nitrogen (volume for volume), does not remain nearest the ground, but is distributed through the air. In a few exceptional localities, carbon dioxide arises from volcanoes faster than it can diffuse, and fills the adjacent valley.

**Argon in the Atmosphere.**—Argon is a colorless, odorless gas. Its chief characteristic is its chemical inactivity. No compounds of argon have as yet been prepared or discovered. The name **argon** is happily chosen, being derived from Greek words signifying **inert**. Four volumes of argon dissolve in 100 volumes of water. Liquid and solid argon have been prepared.

Argon was discovered in 1895 by Rayleigh and Ramsay. Rayleigh had found that nitrogen from air weighed more than an equal volume of nitrogen obtained from compounds of nitrogen. Consequently, they believed that the nitrogen from air contained another gas hitherto overlooked. A series of elaborate experiments showed that after all the oxygen and nitrogen was removed from purified air, there still remained a small quantity of a new gas, which they called argon. It may be prepared (1) by passing pure air over heated copper to remove the oxygen, and then the remaining gas over heated magnesium or calcium to remove the nitrogen; or (2) by passing electric sparks through a mixture of air and oxygen, and removing the compound of oxygen and nitrogen as fast

as it is formed. The latter method is a repetition of the one used by Cavendish when he determined the composition of air, and he would have no doubt discovered argon had he continued his investigations.

**Inert Gases in the Atmosphere.**—Helium, neon, krypton, and xenon have recently been discovered by Ramsay. At present little is known about these gases. They resemble argon in being inactive chemical elements. They constitute an exceedingly minute proportion of the atmosphere. Helium is also found in certain rare minerals, in the gases from some mineral springs, and in the atmosphere of the sun. It is about twice as heavy as hydrogen. According to reliable authority, helium is one of the substances formed by the "decay" of radium. (See Radio-activity.)

**Air is a Mixture**, in spite of the fact that we speak of its "composition." Chemical compounds have two invariable characteristics: viz., (1) their components are in a fixed proportion, and (2) their formation and decomposition are usually attended by definite evidences of chemical action, such as light, heat, change of color and form, etc. The following facts show that air is a mixture of free gases:—

(1) The proportion of oxygen and of nitrogen is not fixed, but varies between small limits, which may be detected by accurate analysis.

(2) When nitrogen and oxygen are mixed in the proportions which form air, the product is exactly like air, but the act of mixing gives no evidence of chemical action.

(3) When air is dissolved in water, a greater proportion of oxygen than of nitrogen dissolves. If the oxygen and nitrogen were combined in the air, the dissolved air would, of course, have the same composition as air itself.

**Liquid Air** is a mixture of the liquefied gases which constituted the air used. It is a milky liquid, owing to the presence of solid carbon dioxide and ice. If these solids are removed by filtering, the filtrate has a pale blue tint. It is slightly heavier than water. It is intensely cold, its

temperature being about  $-200^{\circ}$  C. It boils at about  $-190^{\circ}$  C. under atmospheric pressure. If a tumbler is filled with liquid air, the latter boils vigorously, the surrounding air becomes intensely cold, frost gathers on the tumbler, and in a short time the liquid air will have entirely disappeared into the air of the room. If, however, the liquid air is placed in a Dewar's bulb or flask, it evaporates so slowly that some will remain in the flask several hours.



FIG. 14.—A Dewar's bulb.

many thicknesses of felt and slipped into a larger can covered with canvas or felt. The liquid air is put in the inner can and a loose stopper or piece of felt is placed over the mouth. The liquid may also be kept in these cans for some time with only a moderate loss, unless the surrounding temperature is exceptionally high.

Liquid air, owing to its extremely low temperature, produces remarkable physical changes. A tin or iron vessel which has been cooled by liquid air is so brittle that it may often be crushed with the fingers. Nearly all plastic or soft substances, including many kinds of food, when im-

mersed in liquid air, become hard and brittle, leather being the only important exception. Mercury freezes so hard in liquid air, that it may be used as a hammer to drive a nail. When liquid air is put in a teakettle standing on a block of ice, the liquid air boils vigorously. If the kettle of liquid air is placed over a lighted Bunsen burner, frost and ice collect on the bottom of the kettle, because the intense cold of the kettle solidifies the water vapor and carbon dioxide, which are the two main products of burning illuminating gas. If water is now poured into the kettle, the liquid air boils over and the water is instantly frozen; the water is so much hotter than the liquid air that the latter boils more violently, and since its rapid evaporation causes absorption of heat, the water gives up its heat and becomes ice. Ordinary liquid air is from one half to one fifth liquid oxygen, and will support combustion. A red-hot rod of steel or of carbon burns brilliantly in this cold liquid.

Numerous applications of liquid air have been proposed, but thus far they have not passed the experimental stage. It has been suggested that it be used as a refrigerant instead of ice, for ventilating and cooling rooms, as a blasting material, for removing diseased flesh from a wound, for destroying refuse, and as a commercial source of oxygen. The last use is based primarily on the fact that as liquid air evaporates, the nitrogen passes off first, and in a short time relatively pure oxygen remains (see Oxygen).

A little liquid air was produced in 1883 with considerable labor and at an enormous expense. Now it is easily manufactured in large quantities at a comparatively low cost. In the older methods of preparing liquefied gases, the gas was subjected to tremendous pressure and a low temperature. At present, air (and other gases) is liquefied by a different method. Compressed air cooled by water is forced through a pipe with a valve. As it escapes through the valve, it expands and its temperature falls, because expansion is a cooling process. This cold air is led back over the outside of the same pipe and cools the air inside. This cooling process is continued until finally the air expanding at the valve liquefies in part.

## NITROGEN.

**Occurrence.** — Nitrogen, besides comprising four fifths of the atmosphere, is a component of nitric acid and ammonia, and of the many compounds related to them. It is also an essential constituent of animal and vegetable matter.

The name *nitrogen* was given to the gas by Chaptal from the fact that it is a component of niter, an old name of potassium nitrate.

**Preparation.** — Nitrogen is usually obtained from the air by removing the oxygen by phosphorus. A tall jar is placed over burning phosphorus contained in a shallow dish floating in a large vessel of water. The oxygen combines with the phosphorus, leaving nitrogen, more or less pure, in the jar. Other methods may be used, such as decomposing ammonium nitrite by heat, or passing air over heated copper.

**Additional Properties.** — In addition to its inertness, already mentioned, nitrogen is a little lighter than air, and is very sparingly soluble in water. Its density is 0.972 (air = 1). One liter at 0° C. and 760 mm. weighs 1.2507 gm. One hundred liters of water dissolve only 1.5 l. at the ordinary temperature. It combines with magnesium and a few other metals at a red heat, forming **nitrides**. Electric sparks cause nitrogen to combine with oxygen and with hydrogen, forming ultimately nitric acid and ammonia, hence these substances or others related to them are often found in the rain which falls during a thunder storm.

**Relation of Nitrogen to Life.** — Oxygen, carbon dioxide, and water vapor are essentially related to the life of plants and animals. Nitrogen is also vitally connected with different forms of life. Atmospheric nitrogen merely dilutes the oxygen. Although we live in an atmosphere containing such a large proportion of nitrogen, we cannot assimilate it. According to a reliable authority, "the air as it leaves the lungs contains 79.5 per cent of nitrogen," and hence cannot become a part of the body. Yet all flesh contains nitrogen, and the rejected waste products of ani-

mals are largely combined nitrogen. The nitrogen needed by animals must be in combination to become available. And it is taken in the form of nitrogenous food, such as lean meat, fish, wheat and other grains.

Most plants take up combined nitrogen from the soil in the form of nitrates (compounds derived from nitric acid) or of ammonia. Hence combined nitrogen is being constantly taken from the soil, and in order to preserve the fertility of the soil, nitrogen must be supplied. This is done by allowing nitrogenous organic matter to decay upon the soil, or by adding to the soil a **fertilizer**, which is a mixture containing nitrogen compounds. Recently it has been shown that leguminous plants, such as peas, beans, and clover, take up nitrogen from the air by means of bacteria, which are in nodules on their roots.

#### EXERCISES.

1. What is the atmosphere? What is air? What is the literal meaning of the word *atmosphere*? What is the wind?
2. Develop the topics: (a) atmospheric pressure, (b) occurrence of nitrogen, (c) volumetric composition of the air, (d) gravimetric composition of the air, (e) water vapor in the atmosphere, (f) carbon dioxide in the atmosphere, (g) air is a mixture.
3. Define and illustrate the terms: (a) an atmosphere, (b) normal pressure, (c) standard pressure, (d) dew point, (e) relative humidity, (f) inert.
4. What are the two chief ingredients of the atmosphere? The permanent ingredients? The variable ingredients? The ingredients found in traces? What are sometimes found in the air of cities?
5. What is the symbol of nitrogen? What are its general properties? Its special properties? What is its main function in the atmosphere? How may it be prepared?
6. When and by whom was nitrogen discovered? Why and by whom was it named "azote" and "nitrogen"?
7. What is the relation of nitrogen to animal and to vegetable life?

8. Compare the functions of oxygen and nitrogen in the atmosphere. What famous chemists helped solve this problem?
9. State the composition of pure air (*a*) by volume, and (*b*) by weight.
10. Give a brief biographical account of (*a*) Cavendish, (*b*) Dumas, (*c*) Rutherford. (See Appendix, § 4.)
11. What is a cloud? The dew? Why does moisture gather on cellar walls? Why are mines often damp? What is (*a*) rain, (*b*) fog, (*c*) mist?
12. Describe the action of air upon (*a*) limewater, and (*b*) calcium chloride.
13. How does the atmosphere illustrate the diffusion of gases?
14. What is argon? Give a brief account of (*a*) its discovery, (*b*) its properties, (*c*) its method of preparation. What proportion of pure air is argon? What is the significance of the name *argon*?
15. Give a brief account of helium, neon, krypton, and xenon.
16. What is liquid air? What are its chief properties? State briefly its method of manufacture. Describe its action (*a*) upon solids, such as rubber, (*b*) upon liquids, such as mercury, (*c*) upon hot steel, (*d*) when evaporated quickly. Describe a Dewar's bulb.

### PROBLEMS.

1. If a man inhales 18 cu. ft. of air an hour, what weight of oxygen does he consume in 24 hr.?
2. What is the weight of air in a room,  $6 \times 6 \times 3$  m., if a liter of the air weighs 1.3 gm.?
3. A mixture of 25 cc. of air and 50 cc. of hydrogen is exploded. The residue measures 60.3 cc. What per cent of oxygen did this sample of air contain?
4. How many kilograms of pure air are needed to yield 100 kg. of oxygen?
5. Express in inches the following barometer readings: (*a*) 760 mm., (*b*) 740 mm., (*c*) 75 cm., (*d*) 0.749 m., (*e*) 7.67 dm.
6. Dumas and Boussingault, in 1841, found in a sample of air, 12.373 gm. of nitrogen and 3.68 gm. of oxygen. What per cent of each was found?
7. What is the weight at  $0^{\circ}$  C. and 760 mm. of (*a*) 1000 cc. of dry air? Of (*b*) 750 l., (*c*) 1750 cc., (*d*) 850 cu. m.?

## CHAPTER VII.

### **LAW AND THEORY—LAWS OF DEFINITE AND MULTIPLE PROPORTIONS—ATOMIC THEORY—ATOMS AND MOLECULES—SYMBOLS AND FORMULAS—EQUATIONS.**

**Law and Theory.**—We discover facts by observation and experiment. Facts which always occur under the same circumstances soon become well established. Such facts are often summarized in a brief statement called a law.

Sometimes the word *law* is used in the sense of the uniform behavior summarized in the brief statement. Hence, in a narrow sense, a law is a statement of a fact, but in a broad sense a law is the fact itself. Thus, the law of definite proportions (soon to be discussed) is either (1) a brief statement of the general fact of definite proportions of elements in compounds, or (2) the uniform behavior itself as far as the composition of chemical compounds is concerned.

The cause of many scientific facts is unknown. The explanation we give, or the statement we make, of the cause of facts is called a **theory**. Laws are statements of fact, theories are statements of the supposed cause of facts. Thus we know that chemical compounds have a definite composition, because we have discovered by experiment the facts on which this law is based; and we have framed a **theory**, which, as far as our present knowledge is concerned, is a satisfactory explanation of the cause of the general fact of definite composition. Laws seldom change, but theories are often modified. Laws are the result of experiment, theories are the outcome of mental operations.

We accept a certain theory until a more satisfactory one is proposed. If a fact is not well established or is not general, we account for it by an hypothesis. An hypothesis is a guess or supposition concerning the cause of some particular fact or set of facts, and it is usually proposed as a basis for making further experiments. Hypotheses often lead to theories.

Laws, theories, and hypotheses are of great service in chemistry, since they help us gather into intelligible statements a vast number of facts which are apparently not related. They also assist in discovering facts.

**Law of Definite Proportions by Weight.** — When the metal magnesium is heated in the air, it burns with a dazzling flame into a grayish powder, due to combination with oxygen. If a known weight of magnesium is heated in a crucible, so that the product cannot escape, a remarkable relation is revealed. In order to burn completely 1.5 gm. of magnesium, 1 gm. of oxygen is necessary; and the product, magnesium oxide, weighs 2.5 gm. This product contains, therefore, 60 per cent magnesium and 40 per cent oxygen. Accurate repetitions of this experiment have shown that this proportion by weight is fixed and definite. Again, if all the oxygen is driven from a weighed quantity of potassium chlorate by heating this compound in a crucible, 39.18 per cent of oxygen is always obtained. This means that the proportion of potassium, chlorine, and oxygen which makes up potassium chlorate is fixed and definite. Otherwise, the properties of potassium chlorate would vary. Experiments similar to these show that in all chemical compounds the different components are always present in a definite and unvarying proportion by weight. There are no exceptions to this general fact. This constancy of proportion in

chemical compounds is stated as the **Law of Definite Proportions by Weight**, thus:—

*A given chemical compound always contains the same elements in the same proportions by weight.*

Sometimes it is condensed into this form:—

*A chemical compound has a definite composition by weight.*

This law is one of the fundamental laws of chemistry. It is so firmly believed that if the composition of a compound is found by analysis to vary, chemists conclude that the experimental work is incorrect or that the compound is impure. The law was established as the outcome of a controversy between two French chemists, Proust (1755-1826) and Berthollet (1748-1822). The discussion lasted from 1799 to 1806. Berthollet believed that compounds might have a varying composition. Indeed, by his experiments he detected "gradual changes" in composition. But Proust showed that Berthollet analyzed mixtures and not compounds. In a mixture the parts may be present in any proportion. Subsequent experiments have only strengthened our confidence in this law.

**Law of Multiple Proportions.**—Proust showed that some elements combine in more than one proportion, and thereby produce distinct compounds. But he failed to notice that if the weight of one element is constant, the varying weights of the other element are in a simple multiple relation to each other. Dalton discovered this general fact about 1804. The composition of compounds is usually expressed in per cent; but such expressions in a series of compounds reveal nothing about multiple relations. If, however, a constant weight is adopted as a unit for one component, and the composition of the series of compounds is expressed in terms of this unit, then the simple multiple relation which exists between the weights of the other component is clearly seen. Thus, no multiple relation is apparent in the statement that the two compounds of carbon

and oxygen contain respectively 27.27 and 42.85 per cent of carbon and 72.72 and 57.14 per cent of oxygen. But if we adopt 1 as the weight of carbon, the weights of oxygen are in the simple integral ratio of 2 to 1; i.e. the weights of oxygen are simple multiples. The five compounds of oxygen and nitrogen, which will soon be studied, aptly illustrate multiple proportions:—

TABLE TO ILLUSTRATE MULTIPLE PROPORTIONS.

NAME.	COMPOSITION IN PER CENT.		ADOPTED WEIGHT.	RATIO.	
	Nitrogen.	Oxygen.		Nitrogen.	Oxygen.
Nitrous oxide . . .	63.636	36.363	1	1	0.57
Nitric oxide . . .	46.666	53.333	1	1	1.14
Nitrogen trioxide .	36.842	63.157	1	1	1.71
Nitrogen peroxide .	30.434	69.565	1	1	2.28
Nitrogen pentoxide .	25.925	74.074	1	1	2.85

From this table it is clear that the weights of oxygen combined with the same weight of nitrogen are as 1:2:3:4:5; i.e. they are simple multiples of each other.

The general fact of multiple proportions is expressed in the **Law of Multiple Proportions**, thus:—

*When two (or more) elements unite to form a series of compounds, a fixed weight of one element so combines with different weights of the other element that the relations between the different weights can be expressed by small whole numbers.*

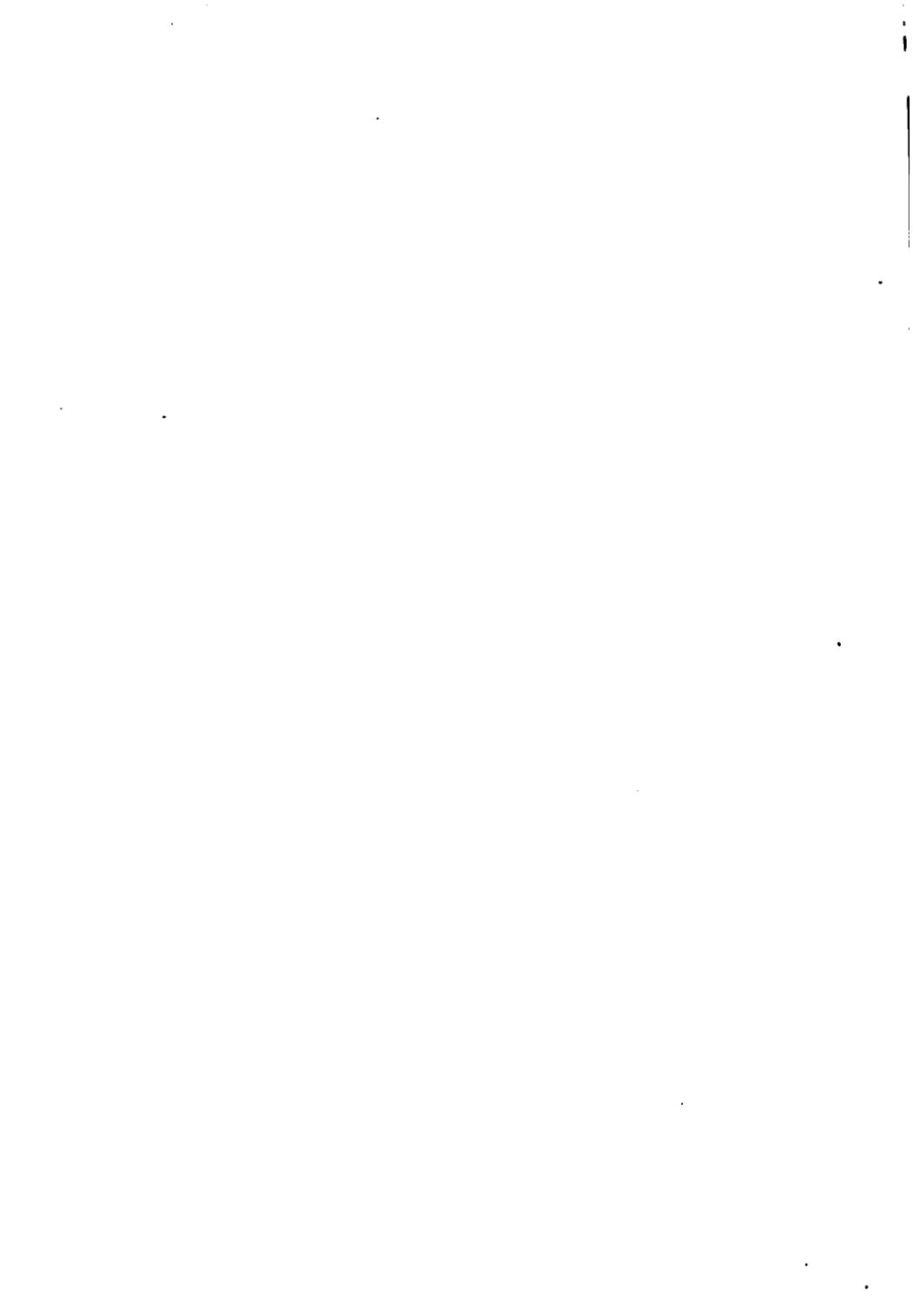
This law, like the law of definite proportions, is a fundamental law of chemistry, and together they have profoundly influenced its theoretical and practical progress.



JOHN DALTON

1766-1844

THE ENGLISH CHEMIST WHO LAID THE FOUNDATIONS OF THEORETICAL CHEMISTRY



The **Atomic Theory** of the constitution of matter was proposed by Dalton to explain the laws of definite and multiple proportions. This theory assumes (1) that the chemical elements and compounds consist ultimately of a vast number of very small particles or **atoms**, (2) that the atoms of the same element have the same weight, (3) that atoms of different elements have different weights, and (4) that chemical action is union or separation of the atoms of the elements.

Let us now consider how this theory explains the facts summarized in the laws of definite and multiple proportions. (1) When magnesium combines with oxygen, 1.5 parts by weight of magnesium combine with one part by weight of oxygen. Analysis of the product — magnesium oxide — shows that this proportion is constant; that is, pure magnesium oxide always contains the elements magnesium and oxygen in this proportion. Now, according to the atomic theory, magnesium oxide is the product of the union of indivisible atoms of magnesium and indivisible atoms of oxygen. It therefore follows that when magnesium and oxygen unite, atom for atom, the magnesium oxide must contain the two elements in the proportion of the weights of their atoms, *i.e.* it must always have the same composition. It is immaterial whether the actual weights of these elements which combine are in the proportion of 1 to 1.5, because whatever is in excess of this proportion will be left uncombined. For example, if we start with 1 gm. of oxygen and 2 gm. of magnesium, then 0.5 gm. of magnesium will be left uncombined. Thus the atomic theory explains the law of definite proportions. (2) But atoms do not always combine in the simple proportion of 1 to 1. They may combine in the proportions of 1 to 2, 2 to 3, 1 to 3, 1 to 4, etc. But according to the atomic

theory atoms are assumed to be indivisible. Hence, if we assume the atomic theory, the proportions of the weights of different elements in a series of compounds must be simple proportions, *i.e.* the elements must unite in accordance with the law of multiple proportions. To illustrate: There are two compounds of carbon and oxygen. In one the ratio of the weight of carbon to oxygen is 3 to 4, and in the other 3 to 8. The second compound contains twice as much oxygen as the first; *i.e.* its molecule contains twice as many atoms of oxygen as a molecule of the first. (Subsequently it will be shown that the first compound is carbon monoxide and contains one atom of oxygen in each molecule, while the second is carbon dioxide and contains two atoms of oxygen in each molecule.) In other words, the weights of oxygen in these compounds are in the ratio of 1 to 2.

**Atoms and Molecules.**—It should not be forgotten that the laws of definite and multiple proportions deal with facts, and that the atomic theory deals with conceptions which may be true, but which cannot be proved to be true. We often speak of atoms as if they could be perceived by the senses, but we do so simply because such expressions help us describe, study, and interpret chemical action. According to the present views, atoms do not, as a rule, exist in the uncombined state. As soon as atoms are freed from combination, they at once unite with some other atom or atoms. The smallest particle of matter which can exist independently is not, therefore, an atom, but a group or combination of atoms. These groups of atoms are called **molecules**. If the atoms in a molecule are atoms of the same element, then the molecule is a molecule of an element; but if the atoms of different elements are combined, then the molecule is the molecule of a compound. All matter, as a rule, consists of mole-

cules, and the molecules are made up of atoms. A molecule of a few elements contains only one atom. Chemists define a **molecule** as the smallest part of a compound or of an element which can exist in the free state and manifest the properties of the compound. Thus, the smallest particle of water is a molecule of water, but a molecule of water contains smaller particles still, viz., atoms of hydrogen and oxygen. We may define an **atom** as the indivisible constituent of a molecule. It is also the smallest particle of an element which takes part in chemical changes.

Our views regarding molecules are based on extensive study of the physical properties of gases. The molecule is often spoken of as the physical unit, because in physical changes molecules are not decomposed. Whereas the atom is the chemical unit, because it enters into all chemical action. The molecule is chemically divisible, but the atom is chemically indivisible.

**Chemical Symbols**, which were mentioned in Chapter I, are designed to represent single atoms. Thus, H represents one atom of hydrogen, O one atom of oxygen, N one atom of nitrogen. If more than one uncombined atom is to be designated, the proper numeral is placed before the symbol, thus :—

2 H means 2 atoms of hydrogen,

3 O means 3 atoms of oxygen,

4 P means 4 atoms of phosphorus.

But if we wish to represent the atoms as in chemical combination, either with themselves or with other atoms, then a subscript is used instead of a coefficient, thus :—

H<sub>2</sub> means 2 atoms of hydrogen in combination,

N<sub>3</sub> means 3 atoms of nitrogen in combination,

P<sub>4</sub> means 4 atoms of phosphorus in combination.

**Chemical Formulas.**—A formula is a group of symbols which is designed to express the composition of a compound. In writing a formula the symbols of the different atoms making up the compound are placed side by side. Thus,  $H_2O$  is the formula of water, because this group of symbols is the simplest expression of the facts which are known about this compound. Similarly,  $KClO_3$  is the formula of potassium chlorate. These symbols might be written in a different order, but usage has determined the order in this, as in most cases. A formula represents one molecule. Hence,  $KClO_3$  represents one molecule of potassium chlorate, and means that the molecule of this compound contains one atom each of potassium and chlorine and three atoms of oxygen. If we wish to designate several molecules, the proper numeral is placed before the formula, thus :—

2  $KClO_3$  means 2 molecules of potassium chlorate.

3  $H_2O$  means 3 molecules of water.

4  $H_2SO_4$  means 4 molecules of sulphuric acid.

In certain compounds some of the atoms act like a single atom in chemical changes. This fact is often expressed by inclosing the group of atoms in a parenthesis, or by separating it from the rest of the formula by a period. Thus, the formula of ammonium nitrate is  $(NH_4)NO_3$ . Similarly, the formula of alcohol is often written  $C_2H_5.OH$ , because the groups  $C_2H_5$  and OH act as units. The use of the period is confined mainly to organic and mineralogical chemistry. It is sometimes omitted, especially if the composition of the compound is well understood. If a group of atoms is to be multiplied, it is placed within a parenthesis. Thus, the formula of lead nitrate is  $Pb(NO_3)_2$ . This means that the group  $NO_3$  is to be multiplied by 2.

The formula  $2 \text{Pb}(\text{NO}_3)_2$  means that the *whole* formula is to be multiplied by 2.

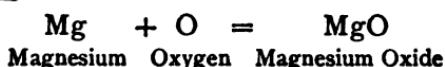
Symbols and formulas are sometimes used to represent an indefinite amount of an element or compound. Thus, O may mean oxygen and  $\text{H}_2\text{SO}_4$  sulphuric acid, regardless of the amount. This use of symbols and formulas saves time, but it is not scientific. They are often thus used to label bottles in a laboratory. Such a departure from accuracy should not be allowed to obscure their real meaning.

The complete significance of symbols and formulas can be grasped only by their intelligent use. They should not be committed to memory slavishly. It is desirable, however, to learn the common ones while the substances they represent are being studied, and consider their relations more fully when the needed facts have accumulated. (See Chapters IX and XIII.)

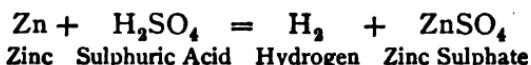
**A Chemical Reaction** is a special or limited chemical change. When potassium chlorate is heated, the chemical change results finally in the liberation of all the oxygen and the formation of potassium chloride. Such a change is called the **reaction** for preparing oxygen from potassium chlorate, or the reaction for the decomposition of potassium chlorate. Obviously, the study of chemistry is largely a study of reactions.

**Chemical Equations.**—In expressing various facts about chemical reactions, it is customary to use an **equation** consisting of the proper symbols or formulas. Substances entering into the initial stage of a reaction are called **factors**, and those present in the final stage are called **products**. The symbols and formulas of the factors connected by the sign plus (+) are placed at the left of the sign of equality, and those of the products at the right. Equations are usually read from left to right. Occasionally the words **reaction** and **equation** are used as synonyms, but such a use is inaccurate and confusing.

When magnesium burns in the air or in oxygen, magnesium oxide is formed. The simplest equation for this reaction is —



This equation is read : Magnesium and oxygen form magnesium oxide. It means, also, that when magnesium and oxygen react, one atom of magnesium unites with one atom of oxygen and forms one molecule of magnesium oxide. The simplest equation for the preparation of hydrogen by the reaction of zinc and sulphuric acid is —



This equation is read: Zinc and sulphuric acid form (or produce) hydrogen and zinc sulphate. It means, further, that one atom of zinc and one molecule of sulphuric acid form one molecule (or two atoms) of hydrogen and one molecule of zinc sulphate. By similar equations we may express certain facts about all reactions which are understood. The above equations might be called **ordinary chemical equations**, or atomic equations. Other forms are used, and they will be discussed in Chapters IX, X, and XIII.

The following facts about ordinary chemical equations should be noted : —

(1) The sign plus does not necessarily mean addition *chemically*. It does in the equation  $\text{Mg} + \text{O} = \text{MgO}$ , but not in the equation  $\text{HgO} = \text{Hg} + \text{O}$ . In the latter the products are merely mixed.. The sign plus may be expressed by the words *and*, *acted upon*, *added to*, *mixed with*. The sign equality is often read *equal*, *give*, *form*, or *produce*.

(2) Equations do not always include all the participating substances. In  $\text{Mg} + \text{O} = \text{MgO}$  no nitrogen (N) appears because nitrogen takes no

chemical part in the change, despite the fact that the air is largely nitrogen. Similarly, in  $Zn + H_2SO_4 = H_2 + ZnSO_4$ , no water ( $H_2O$ ) appears, because the water (in the dilute sulphuric acid) simply serves to dissolve the zinc sulphate from the surface of the zinc. A special form of equation, called the ionic equation, is used to express chemical changes which occur in solution (see Chapter X).

- (3) Equations tell nothing about the heat changes (see Chapter X).
- (4) Most equations represent only the beginning and end of reactions. Thus, in  $KClO_3 = 3 O + KCl$  several changes do not appear, because the purpose of this equation is to express the complete decomposition of potassium chlorate — nothing else.

### EXERCISES.

1. Define law, theory, and hypothesis as used in science.
2. State the law of definite proportions. Illustrate it. Give a brief account of its discovery.
3. State the law of multiple proportions. Illustrate it. Who discovered it? When?
4. State the atomic theory. What are atoms according to this theory? How are atoms related to chemical action? How are atoms related to molecules? What is a molecule?
5. What is the symbol of an element? How are they formed? Interpret the symbols: H, 2 O, N<sub>2</sub>, 2 P, 3 O, K, S, 2 Cl.
6. What is the formula of a compound? What does a formula represent? Interpret the formulas:  $H_2O$ , 2  $H_2O$ ,  $KClO_3$ , 4  $H_2SO_4$ ,  $(NH_4)NO_3$ ,  $C_2H_5 \cdot OH$ ,  $Pb(NO_3)_2$ ,  $Ca(OH)_2$ .
7. Give the symbols of the following elements: oxygen, hydrogen, nitrogen, zinc, copper, magnesium, platinum, iron, sodium, sulphur, carbon, mercury.
8. What elements correspond to the following symbols: Na, Cu, K, Zn, S, P, Pt, Pb, H, Hg, Fe, Mg? (See App., § 5.)
9. Give the formulas of the following compounds: water, potassium chloride, sulphuric acid, magnesium oxide.
10. Define and illustrate the term *chemical reaction*.
11. What is a chemical equation? For what is it used? What are factors and products in an equation? How are equations written? Illustrate your answer. How are they read?

12. Interpret the equation:  $Mg + O = MgO$ .
13. What does the plus (+) sign mean in the above equation? What other meanings has this sign?
14. State several facts about equations.

#### PROBLEMS.

1. How many centigrams in 1745 kg.? In 250 gm.? In 1425 dg.?
2. How many cubic centimeters in 50 l.? In 1 cu. dm.?
3. What is the weight of (a) 100 cc. of hydrogen, and (b) 25 l. of oxygen, under standard conditions?
4. What weight of (a) hydrogen and (b) oxygen can be obtained from 180 gm. of water?
5. What (a) weight and (b) volume of oxygen are necessary to unite with 200 kg. of hydrogen?
6. What weight of hydrogen is necessary to unite with the oxygen in 100 gm. of air to form water? (Assume that air is one fifth oxygen.)

## CHAPTER VIII.

### ACIDS, BASES, AND SALTS.

**Introduction.** — Many chemical compounds fall naturally into one of three groups, long known as acids, bases, and salts. Not all compounds, of course, are included in this classification. Each group has its characteristic properties, though the groups are closely related and sometimes overlap. Many familiar substances belong to these groups. A knowledge of the properties of acids, bases, and salts, of their special behavior, and of their intimate relations is essential in the study of chemistry.

**General Properties of Acids, Bases, and Salts.** — Acids have a sour taste. The early chemists detected this property, and the word *acid* (from the Latin *acidus*, sour) emphasizes the fact. Acids change the color of many vegetable substances. Thus, blue litmus is turned red by acids. Acids also have the power to decompose most carbonates, like limestone, thereby liberating carbon dioxide gas which escapes with effervescence. Most bases have a slimy, soapy feeling, and a bitter taste. They turn red litmus blue. Caustic soda and ammonium hydroxide are bases. Many salts have the well-known salty taste. Sodium chloride, the familiar table salt, is an example. Usually, they have no action on litmus.

**Composition of Acids, Bases, and Salts.** — Acids contain hydrogen, which is usually liberated when metals and acids interact. It was long thought that oxygen was an

essential component of all acids, and its name, *oxygen* (derived from Greek words meaning "acid producer") was given by Lavoisier because of this belief (see Discovery of Oxygen).

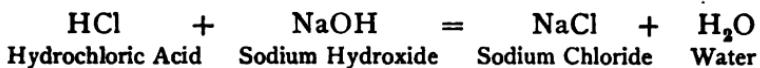
We now know that hydrogen, not oxygen, is the essential component of all acids. Another necessary component of acids is some element like nitrogen, sulphur, chlorine, or phosphorus, which belongs to a class of elements called **non-metals**. For this reason it is sometimes convenient to think of non-metals as the elements which form acids. Thus sulphuric acid contains sulphur, besides hydrogen and oxygen; while hydrochloric acid contains chlorine, besides hydrogen.

Bases contain hydrogen and oxygen besides a metal. The hydrogen and oxygen are the essential components (see Hydroxyl, below). It is often convenient, however, to regard metals as the elements which form bases, just as the non-metals form acids. Thus, the base sodium hydroxide contains the metal sodium besides hydrogen and oxygen.

Salts contain a metal and a non-metal, and most of them contain oxygen. Thus, potassium nitrate contains the metal potassium and the non-metal nitrogen, besides oxygen; while potassium chloride contains potassium and the non-metal chlorine, but no oxygen. (See Salts, below.)

**Neutralization.** — The nature of acids, bases, and salts is shown by their chemical relations. When acids and bases interact, salts are formed. That is, the acid and base destroy more or less completely the marked properties of each other and produce a compound which has few, and often none, of the properties of the original acid or base. The acid and base **neutralize** each other. An example will make this point clear. When hydrochloric

acid and sodium hydroxide interact, sodium chloride and water are formed. The chemical change may be written thus—



This equation represents the facts which have been repeatedly verified by experiment. This kind of a chemical change is called **neutralization**, and later it will be more fully discussed. Taking this equation as a type of the chemical changes which occur in neutralization, it is clear that in such changes, generally speaking (1) the metal of the base takes the place of the hydrogen of the acid, thereby forming a salt, while (2) the hydrogen of the acid combines with the hydrogen and oxygen of the base to form water. In neutralization the hydrogen and oxygen of the base act as a unit. This group of atoms (OH) is called **hydroxyl**. Compounds containing this group are called **hydroxides**. Hydroxyl does not exist free and uncombined like elements and compounds, but it acts like a single atom in many changes. It is called a **radical**. To emphasize the fact that it is a unit, the hydroxyl group is sometimes put in a parenthesis, *e.g.*  $\text{Ca(OH)}_2$ .

The nature of acids, bases, and salts is further shown by the behavior of their solutions toward electricity. All such solutions conduct electricity, and therefore, according to the theory of electrolytic dissociation, the solutions contain ions. Thus, solutions of acids contain hydrogen ions and non-metallic ions, solutions of bases contain hydroxyl and metallic ions, and solutions of salts contain, as a rule, neither hydrogen nor hydroxyl ions, but metallic and non-metallic ions. Many facts agree with these theoretical views, and it is very generally believed that the general properties of acids, bases, and salts, as well as the chemical changes which occur in neutralization, are due to ions. (See also Neutralization, below.)

**Acids.** — The common acids are sulphuric acid, hydrochloric acid, nitric acid, and acetic acid. Many acids are liquid, as sulphuric and nitric; a few are gases, as hydrochloric; others are solid, as tartaric, citric, oxalic. Most are soluble in water, and such solutions are familiarly called acids. These solutions may be dilute or concentrated, and the general properties vary somewhat with the strength. Concentrated acids are usually corrosive and should be handled with precaution, even when one is thoroughly familiar with their properties. Substances which turn blue litmus to red are said to contain an acid, to be acid, or to have an acid reaction. The exact nature, however, of such a substance must be determined by additional tests.

Many familiar substances are acids or contain them. Vinegar, pickles, and similar relishes contain dilute acetic acid. Lemon juice is mainly citric acid. Sour milk contains lactic acid. Unripe fruits, sour bread, and sour wines contain acids. "Soda water" is a solution of carbonic acid (or more accurately carbon dioxide), and "acid phosphate" is a solution of a sour calcium phosphate.

Formerly acids were defined as compounds producing a sour solution which reddens blue litmus, or as compounds which form salts by interaction with bases, or as compounds containing hydrogen which can be replaced by a metal. These definitions emphasize certain properties of acids, but they are not inclusive. According to the theory of electrolytic dissociation an acid is a compound whose solution contains hydrogen ions. The sour taste, behavior toward litmus, and liberation of hydrogen — properties which are common to all acids — are due to the hydrogen ions in the acid solution.

**Nomenclature of Acids.** — Oxygen is a component of most acids, and the names of these acids correspond to the proportion of oxygen which they contain. The best known acid of an element usually has the suffix **-ic**, e.g. sulphuric, nitric, phosphoric. If an element forms another acid, containing less oxygen, this acid has the suffix **-ous**, e.g. sulphurous, chlorous, phosphorous. Some elements form an acid containing less oxygen than the **-ous** acid; these acids retain the suffix **-ous**, and have, also, the prefix **hypo-**, e.g. hyposulphurous, hypophosphorous, hypochlorous. Hypo- means under or lesser. If an element forms an acid containing more oxygen than the **-ic** acid, such an acid retains the suffix **-ic**, and has, also, the prefix **per-**, e.g. persulphuric, perchloric. The prefix **per-** means beyond or over. The few acids which contain no oxygen have the prefix **hydro-** and the suffix **-ic**, e.g. hydrochloric, hydrobromic, hydrofluoric. It should be noticed that these suffixes are not always added to the name of the element, but often to some modification of it.

The nomenclature of acids is well illustrated by the series of chlorine acids : —

#### ACIDS OF THE ELEMENT CHLORINE.

NAME.	FORMULA.
Hydrochloric	HCl
Hypochlorous	HClO
Chlorous	HClO <sub>2</sub>
Chloric	HClO <sub>3</sub>
Perchloric	HClO <sub>4</sub>

Not all elements form a complete series of acids, but the nomenclature usually agrees with the above principles.

Some acids have commercial names. Thus, sulphuric acid is often called oil of vitriol, and hydrochloric acid is known as muriatic acid. Acids in which carbon is the essential component end in -ic, but they are often arbitrarily named (see Organic Acids).

An examination of the formulas of acids shows that all do not contain the same number of hydrogen atoms. Acids are sometimes classified by the number of hydrogen atoms which can be replaced by a metal. This varying power of replaceability is called **basicity**. A **monobasic acid** contains only one atom of replaceable hydrogen in a molecule, *e.g.* nitric acid,  $\text{HNO}_3$ . A molecule of acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ) contains four atoms of hydrogen, but for reasons which are too complex to state here, only one of these atoms can be replaced by a metal. **Dibasic** and **tribasic acids** contain two and three replaceable hydrogen atoms, *e.g.* sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ). Obviously, monobasic acids form only one class of salts, dibasic acids form two classes, tribasic acids form three, and so on.

**Bases.** — The term *base*, in a narrow sense, means the strong bases, which are very soluble in water, and are commonly known as **alkalies**, *e.g.* sodium, potassium, and ammonium hydroxides. Formerly the term *base* meant a substance which will neutralize an acid, *e.g.* calcium oxide, ammonia gas, as well as the hydroxides of metals. Most bases are solids; but since they are usually soluble in water, these solutions, as in the case of acids, are familiarly called the base, or alkali, itself. Concentrated alkalies, like concentrated acids, are corrosive. The common alkalies — sodium and potassium hydroxides — are often called caustic soda and caustic potash to emphasize this property; and calcium oxide, or lime, is sometimes called caustic lime; the corrosive nature of ammonium hydroxide, or ordinary ammonia, is also well known. Substances which turn red litmus to blue are said to contain an **alkali** (or base), to be **alkaline**, or to have an **alkaline** reaction.

The word **basic** is often used instead of alkaline. Other tests besides that with litmus must be applied, however, to determine the exact nature of a substance having an alkaline reaction. Alkalies dissolve grease and fats, and are often used as cleansing agents, ammonium hydroxide being widely employed for this purpose. They also interact with fats to form soaps, large quantities of sodium hydroxide being annually utilized in the soap industry (see Soap).

A base was formerly defined as a compound which has a bitter taste, turns red litmus blue, and neutralizes acids. This definition emphasizes certain properties of a base, but it is defective. According to the theory of electrolytic dissociation, a base is a compound whose solution contains hydroxyl ions. The characteristic properties are ascribed to the hydroxyl ions which are common to all solutions of bases.

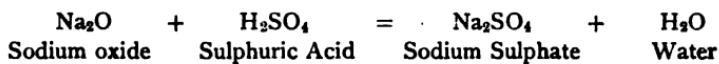
**Nomenclature of Bases.** — There is no general rule covering the nomenclature of bases, as in the case of acids. Since every base contains hydrogen and oxygen, they are often called **hydroxides**. **Hydrate** is sometimes used as a synonym of hydroxide. The term *alkali* emphasizes general properties rather than suggests specific composition. Hydroxides are distinguished from each other by placing the name of the metal before the word **hydroxide**, e.g. sodium hydroxide, potassium hydroxide, calcium hydroxide. The common hydroxides have long been known by several names. Thus, calcium hydroxide is often called limewater. Ammonium hydroxide is sometimes called ammonia water or simply (but inaccurately) ammonia, and it was formerly called volatile alkali. Besides the common names of the hydroxides of sodium and potassium already given, they are sometimes called fixed alkalies.

Not all bases contain the same number of hydroxyl groups. Hence bases, like acids, may form one or more salts. This power is called **acidity**. Bases are called **monacid**, **diacid**, **triacid bases**, etc., according to the number of replaceable hydroxyl groups present in a molecule. Thus, calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is a diacid base, and aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) is a triacid base.

**Salts.** — Sodium chloride is the most familiar salt. Most salts are soluble in water, and their solutions have varied properties. As to taste, they may be salty, bitter, astringent, sour, or flat. Many have no action on litmus and are said to be **neutral** or to have a **neutral reaction**; some turn red litmus to blue, and others turn blue to red. The term **neutral** is also applied to any substance whose solution is indifferent to litmus. Solutions of salts conduct electricity.

Salts invariably contain a metal and a non-metal. Many also contain oxygen. One class contains hydrogen besides oxygen and the characteristic metal and non-metal. From the standpoint of neutralization salts are compounds formed either by the substitution of a metal for all or part of the hydrogen of an acid or by the substitution of a non-metal (or non-metallic group, like  $\text{SO}_4$ ) for all or some of the hydroxyl groups of a base. According to the theory of electrolytic dissociation a salt may be defined as a compound formed by the union of the metallic ion of a base with the non-metallic ion of an acid. (See Normal, Acid, and Basic Salts, below.)

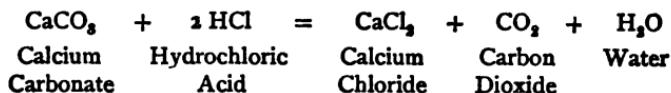
Salts are formed in various ways. The interaction of an acid and a base has been mentioned. The interaction of acids with oxides of certain metals or with metals themselves produces salts. Sodium oxide and sulphuric acid interact and form the salt sodium sulphate, thus :—



While zinc and sulphuric acid, as already stated, form the salt zinc sulphate as well as hydrogen, thus :—



Carbonates interact with acids and form other salts. Calcium carbonate and hydrochloric acid form the salt calcium chloride, thus :—



**Nomenclature of Salts.** — The name of salts containing oxygen are derived from the name of the corresponding acid. The characteristic suffix of the acid is changed to indicate this relation. Thus, the suffix -ic becomes -ate, and the suffix -ous, becomes -ite. Hence :—

Sulphuric acid forms **sulphates**.

Sulphurous acid forms **sulphites**.

Nitric acid forms **nitrates**.

Nitrous acid forms **nitrates**.

Chloric acid forms **chlorates**.

Hypochlorous acid forms **hypochlorites**.

Permanganic acid forms **permanganates**.

The name of the replacing metal is retained, e.g. potassium chlorate, sodium sulphate, calcium hypochlorite, potassium permanganate. Notice that the prefixes *hypo-* and *per-* are not changed.

The names of salts containing only two elements, following the general rule for binary compounds, end in -ide. This suffix is added to a modification of the name of the non-metal, giving the names chloride, bromide, sulphide, fluoride, etc. The prefix *hydro-* which is contained in the

name of the acid is omitted. Thus, the name of the sodium salt of hydrochloric acid is sodium chloride; similarly, there are the names potassium chloride, calcium fluoride, and sodium iodide. Sometimes, the salts of these hydrogen acids are called **halides** to emphasize their relation to common salt, which in Greek is called *halos*.

Salts in which all the hydrogen atoms of the corresponding acid have been replaced by a metal are called **normal salts**, e.g. sodium sulphate,  $\text{Na}_2\text{SO}_4$ . If some of the hydrogen atoms are not replaced by a metal, an **acid salt** is formed. Thus, acid sodium sulphate may be regarded as derived from sulphuric acid, which is dibasic, by replacing one of the atoms of hydrogen by sodium, though of course the salt is not prepared in this way. Expressed as formulas these relations may be written thus:—

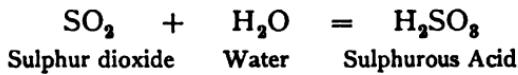
Acid	Acid Salt	Normal Salt
$\text{H}_2\text{SO}_4$	$\text{HNaSO}_4$	$\text{Na}_2\text{SO}_4$

Only those acids which contain two or more replaceable hydrogen atoms form acid salts. On the other hand, if not all the hydroxyl groups of a base are replaced when the base reacts with an acid, then a **basic salt** results. Thus, basic nitrate of bismuth may be regarded as the salt derived from bismuth hydroxide ( $\text{Bi}(\text{OH})_3$ ) by replacing one hydroxyl group of the base by the group  $\text{NO}_3^-$  of nitric acid. The formula of this basic nitrate of bismuth is  $\text{Bi}(\text{OH})_2\text{NO}_3$ .

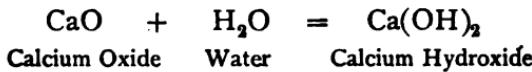
Solutions of many normal salts contain neither hydrogen nor hydroxyl ions, according to the theory of electrolytic dissociation, and hence are neutral to litmus; a few are exceptional. (See Hydrolysis.) But solutions of acid salts or basic salts contain not only the ions characteristic of a salt, but also hydrogen ions or hydroxyl ions. Hence acid salts redden blue litmus and basic salts (if they are soluble) act oppositely.

**Relation of Oxides to Acids and Bases.**—Most non-metallic elements form oxides which unite with water and produce an acid. The oxides of many metallic elements,

on the other hand, unite with water and produce hydroxides. The two oxides of the non-metal sulphur act thus—



The oxide of the metal calcium acts thus—



Oxides of non-metals which unite with water and produce acids are called **acid anhydrides**, *i.e.*, literally, substances *without water*. Examples are carbonic anhydride ( $\text{CO}_2$ ), sulphuric anhydride ( $\text{SO}_3$ ), phosphoric anhydride ( $\text{P}_2\text{O}_5$ ). Oxides of metals which produce bases are called **basic anhydrides**. A few oxides behave exceptionally. It is convenient to regard an acid anhydride as the root or basis of its corresponding acid, and a basic anhydride as the root of its hydroxide.

The fact that many non-metallic oxides redden moist blue litmus led Lavoisier into the erroneous belief that oxygen is an essential component of acids. And some authorities even now (incorrectly) speak of these oxides as acids; thus, carbon dioxide ( $\text{CO}_2$ ) is occasionally called carbonic acid. The compounds which Lavoisier called acids were anhydrides. And it was not until about 1811 that Davy showed (1) that some acids do not contain oxygen (*e.g.* hydrochloric acid,  $\text{HCl}$ ), and (2) that the so-called acids of Lavoisier are not real acids until they have obtained hydrogen from the water in which they dissolve.

**Neutralization** has been defined as the series of changes whereby acids and bases mutually destroy each other's characteristic properties and produce a salt and water.

But neutralization has a deeper meaning and broader application than the mere destruction of properties. (See page 127.)

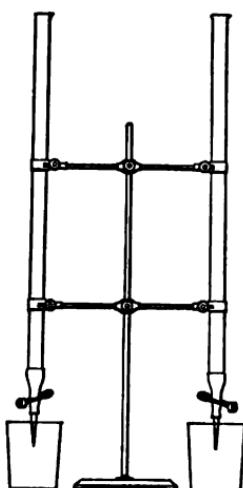


FIG. 15.—Burettes.

If measured volumes of different acids are exactly neutralized by different alkalies, remarkable relations are revealed. This may be done by dropping one into the other from a graduated tube, called a burette (Fig. 15). The exact point of neutralization is shown by an indicator; this is a solution of litmus or some other substance, which tells by the color whether the solution is acid or alkaline. Experiment shows that (1) a definite quantity of an acid neutralizes a definite quantity of an alkali, (2) the same acid is neutralized by different quantities of different alkalies, and (3) the ratio of the quantities of the different alkalies is the same for all acids.<sup>1</sup>

#### EXERCISES.

1. Define and illustrate (*a*) an acid, (*b*) a base, (*c*) a salt, (*d*) an alkali, (*e*) hydroxyl, (*f*) an hydroxide.
2. Name three common acids and bases. State the general properties of each class.
3. Define and illustrate (*a*) neutralization, (*b*) acidity of bases, (*c*) basicity of acids, (*d*) normal, acid, and basic salts, (*e*) caustic alkali, (*f*) radical.
4. What is the literal meaning of (*a*) acid (adj.), (*b*) caustic, (*c*) per-, (*d*) hypo-, (*e*) anhydride?
5. Name the sodium salt of hydrochloric acid. Name the corresponding salt of potassium, lead, calcium, barium, zinc, silver.
6. Name the same salts of nitric acid. Of nitrous acid.
7. Name the same salts of sulphuric acid. Of hypochlorous acid. Of perchloric acid.

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<sup>1</sup> A more extended treatment of this subject may be found in the author's "Experimental Chemistry," pp. 124 ff.

8. Name the hydroxides corresponding to sodium, potassium, calcium, barium, zinc, lead, copper.

9. Name the potassium salt of manganic acid, calcium salt of hydrofluoric acid, sodium salt of carbonic acid, potassium salt of tartaric acid, lead salt of chromic acid, potassium salt of hydrobromic acid, potassium salt of permanganic acid.

**PROBLEMS.**

Review any of the preceding problems, especially those in Appendix, § 1.

## CHAPTER IX.

### EQUIVALENTS—ATOMIC AND MOLECULAR WEIGHTS— CHEMICAL CALCULATIONS—QUANTITATIVE SIGNIFICANCE OF EQUATIONS.

**Equivalents.**—The equivalent or equivalent weight of an element is that weight which is chemically equivalent to one part by weight of hydrogen. More specifically, it is the number of grams of an element which liberates, replaces, or combines with 1 gm. of hydrogen. Experiments show that approximately 32.5 gm. of zinc will liberate 1 gm. of hydrogen from an acid. Hence 32.5 is the equivalent of zinc. Similarly, 23 gm. of sodium liberate 1 gm. of hydrogen from water. A summary of numerous experiments reveals the following —

TABLE OF EQUIVALENTS.

ELEMENT.	EQUIVALENT.
Hydrogen	1 (by definition)
Oxygen	8
Chlorine	35.5
Bromine	80
Sulphur	16
Zinc	32.5
Copper	31.7
Magnesium	12
Sodium	23
Potassium	39
Silver	108
Aluminium	9

Analysis of chemical compounds determines the proportion of their components by weight. And in many cases such experiments verify the equivalents found by other methods. Thus, experiment shows that—

35.5 parts of chlorine unite with 23 of sodium, or 39 of potassium.

80 parts of bromine unite with 23 of sodium, or 39 of potassium.

108 parts of silver replace 23 of sodium, or 39 of potassium.

The above elements always unite in these proportions. But some elements unite in several proportions. Thus, eight parts by weight of oxygen combine with one part of hydrogen to form water. But in a large number of compounds sixteen parts of oxygen combine with various parts of different elements. Similarly, nitrogen unites in the proportion of fourteen, twenty-eight, and forty-two parts by weight with different parts of other elements. In a word, there are **multiples of equivalents**. Comparison shows a striking coincidence between many equivalent weights and the accepted atomic weights of the same elements. This topic is discussed and applied in Chapter XIII.

**Atomic Weights.**—The essential property of matter is weight. According to the atomic theory, atoms have weight. But the absolute weight of an atom cannot be determined directly by any instruments available. We can, however, find the relative weight of an atom; that is, how many times heavier one atom is than another atom. If we adopt one as the weight of an atom of hydrogen, the weights of atoms of other elements can be readily expressed in terms of this standard. Thus, when we say the atomic weight of sodium is twenty-three, we mean that an atom of sodium weighs twenty-three times as much as an atom

of hydrogen. The relative weights are called the **atomic weights of the elements**.

The determination of the atomic weight of an element is a difficult task. Many principles influence the final selection of the number adopted as the atomic weight. We have already seen that there is a definite relation between the equivalent weight and the atomic weight of an element. But this method cannot be used exclusively to determine the atomic weights of elements, because several elements have more than one equivalent. There is also a definite relation between the molecular weight of a compound and the atomic weights of the elements in the compound. These topics and others related to them will be discussed in Chapter XIII. For the present, the approximate atomic weights found in the Appendix, § 5, may be used in solving problems and for general reference.

The atomic weights are not necessarily whole numbers, but they are nearly so in many cases, and for most purposes round numbers may be used. Different atomic weights are sometimes given for the same element. This is due (1) to the disagreement among chemists as to the accuracy of certain results, and (2) to the use of several standards for reckoning atomic weights. For many years hydrogen was the standard. But for scientific reasons oxygen has been adopted as the standard, and 16 is accepted as its atomic weight. This change does not alter the fact; it merely changes the relative values of the atomic weights. Thus, the atomic weight of hydrogen becomes 1.008, if oxygen equals 16, and others are proportionally changed. (See Appendix, § 5.)

**Symbols and Atomic Weights.**—Symbols not only represent atoms, but they express atomic weights. Thus, O represents one atom of oxygen, but it also means that this atom weighs sixteen times more than an atom of hydrogen. Similarly, K represents an atom of potassium, which weighs thirty-nine times more than an atom of hydrogen.

**Molecular Weights.**—Since atoms combine to form molecules, a molecular weight is the sum of the weights of the atoms in a molecule. A molecule of nitric acid contains one atom each of hydrogen and nitrogen, and three atoms of oxygen; hence its molecular weight is  $1 + 14 + 16 \times 3 = 63$ . Given the formula, the molecular weight is easily found by adding the atomic weights. The molecular weight and formula of a compound, therefore, are rigidly connected; and just as a symbol stands for an atomic weight, so a formula expresses a molecular weight. Molecular weights of compounds are conveniently found by adding the weights of the atoms in a molecule, but they are not actually determined in this way.

Many facts and principles determine the final selection of the molecular weight, and hence the formula, of a compound. These will be discussed in Chapter XIII.

**Chemical Calculations** are largely based on atomic and molecular weights.

*Percentage Composition.*—Since the formula of a compound expresses its composition, it is possible to calculate from the formula the composition in per cent. The formula of sulphuric acid is  $H_2SO_4$ , and its molecular weight is 98, i.e.  $2 + 32 + 64$ . The calculations are most easily made by the following proportions:—

$$2 : 98 :: x : 100, \quad x = 2.04 \text{ per cent of hydrogen.}$$

$$32 : 98 :: x : 100, \quad x = 32.65 \text{ per cent of sulphur.}$$

$$64 : 98 :: x : 100, \quad x = \underline{65.31 \text{ per cent of oxygen.}}$$

Total 100.00 per cent.

By the same method the percentage composition of any compound may be calculated.

*Simplest Formula.*—The simplest formula of a compound may be found by dividing the percentage of each element in the compound by its atomic weight. The percentage composition of sulphuric acid is H = 2.04, S = 32.65, O = 65.31. Dividing each percentage by the atomic weight of the element, we have (approximately)  $2.04 + 1 = 2$ ,  $32.65 + 32 = 1$ ,  $65.31 + 16 = 4$ . Hence the simplest formula of sulphuric acid is  $\text{H}_2\text{SO}_4$ . Sometimes the products of the percentages divided by the atomic weights are not whole numbers. In that case the simplest relation is found by proportion. The following problem illustrates this principle: the percentage composition of a compound is C = 40, H = 6.67, O = 53.33. Dividing as above, we have  $40 + 12 = 3.33$ ,  $6.67 + 1 = 6.67$ ,  $53.33 + 16 = 3.33$ . But 3.33, 6.67, 3.33 are in the same proportion as 1 : 2 : 1. Hence the simplest formula is  $\text{CH}_2\text{O}$ .

**Making Equations.**—Chemical reactions may be expressed by equations (see page 83). One method of working out certain chemical equations is very simple.

It has already been stated that the equation for the reaction between magnesium and oxygen is—



This equation is the outcome of the following: it can be readily shown by experiment that when magnesium is heated in air or oxygen, the magnesium and oxygen combine in the ratio 3 : 2. Now results like this are usually expressed in terms of the atomic weights of the reacting elements. But we do not know the number of atomic weights of these elements which must be taken to produce the ratio 3 : 2. That is, we do not know whether the ratio requires the atomic weight or some multiple of it.

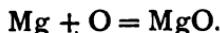
But if we let  $y$  equal the unknown number of atomic weights of magnesium and  $z$  the unknown number of atomic weights of oxygen, then we can write the preliminary equation thus—

$$y \times \text{at. wt. of mag.} : z \times \text{at. wt. oxygen} = 3 : 2.$$

The atomic weight of magnesium is 24 and of oxygen is 16. Therefore the problem reduces itself to finding the values of  $y$  and  $z$  in the equation—

$$y \times 24 : z \times 16 = 3 : 2.$$

By inspection  $y = z$ , and the simplest value of each is 1. Now the symbol Mg stands for 24 parts of magnesium and O for 16 parts of oxygen. That is, Mg not only means one atom of magnesium, but also that this atom weighs 24, if one atom of oxygen weighs 16. Therefore Mg and O are the symbols representing the smallest number of atoms which are equivalent arithmetically to the ratio 3 : 2. The formula of the product of their combination is MgO, and the simplest equation is—



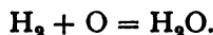
Again, suppose we wish to find the correct equation for the reaction between hydrogen and oxygen in the formation of water. Experiment shows that hydrogen and oxygen combine in the ratio of 1 : 8 by weight. Pursuing the same line of argument as above, we let  $y$  equal the unknown number of atomic weights of hydrogen, and  $z$  that of oxygen. The preliminary equation is—

$$y \times \text{at. wt. of hydrogen} : z \times \text{at. wt. of oxygen} = 1 : 8.$$

The atomic weight of hydrogen is 1 and of oxygen is 16. The equation now becomes—

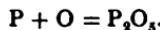
$$y \times 1 : z \times 16 = 1 : 8.$$

By inspection  $y = 2z$ , and the simplest values are  $y = 2$  and  $z = 1$ . Now the symbol H stands for 1 part hydrogen and O for 16 parts of oxygen. Therefore,  $2H$  and  $O$  represent the smallest number of atoms equivalent arithmetically to the ratio 1 : 8, found by experiment. The formula of the product of their combination is  $H_2O$ , and the simplest equation is —



By a similar argument many simple chemical equations may be developed.

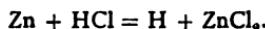
**Another method** is often possible. When we know the factors and products of a reaction, we can find their symbols or formulas in the book, construct a preliminary equation, and then balance the equation; *i.e.* select the proper coefficients, subscripts, or both, so that there shall be an equal number of atoms of each element on both sides of the equation. An example will make this method clear. When phosphorus burns in oxygen, phosphorus pentoxide is formed. The preliminary equation is —



Here it is evident that to balance the equation we need 2 P and 5 O on the left. Hence the final equation is —



Again, when zinc and hydrochloric acid interact, hydrogen and zinc chloride are formed. The preliminary equation made from the symbols and formulas is —

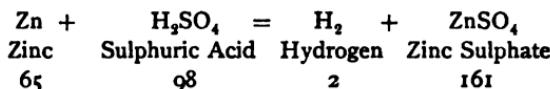


By inspection, it is evident that two atoms of chlorine are on the right and only one on the left. To obtain  $Cl_2$  it is necessary to write 2 HCl. But 2 HCl means not only 2 Cl but 2 H. Hence the equation becomes —



A final inspection shows that an equal number of atoms of each element is on both sides of the equation.

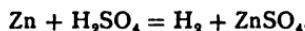
**Problems based on Equations.** — Since equations are expressions of chemical reactions which involve no loss in weight, it is possible to solve many problems connected with reactions. An equation states the proportions which participate in a reaction. Obviously, any convenient weights of zinc and sulphuric acid might be allowed to interact, but the factors and products are always in the proportions given in the equation —



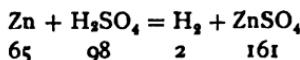
This expression means that 65 parts of zinc always interact with 98 parts of sulphuric acid and yield 2 parts of hydrogen and 161 parts of zinc sulphate. For parts we may read grams, ounces, kilograms, — any unit, — but the same unit must be used throughout the calculations. Therefore, if we know the weight of one substance participating in a reaction, all other weights involved may be readily calculated.

Suppose 45 gm. of zinc interact with sulphuric acid ; the weights of (a) acid required, (b) hydrogen formed, and (c) zinc sulphate produced are calculated as follows : —

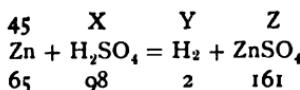
(1) Write the chemical equation for the reaction, thus : —



(2) Place under each term of the equation its atomic or molecular weight,<sup>1</sup> as the case may be, thus : —



(3) Place above the proper terms the known weight and required weight (*i.e.* X, Y, Z, etc.) involved in the problem, thus : —



<sup>1</sup> The atomic weights are given in the table in the Appendix, § 5. Molecular weights are obtained by adding the proper atomic weights.

(4) State in the form of a proportion the four terms involved, remembering that the known and required weights are in the same ratio as the atomic and molecular weights. Thus, the three proportions in the given problem are :—

- (a)  $45 : X :: 65 : 98$ ;  $X = 67.8$  gm. sulphuric acid.
- (b)  $45 : Y :: 65 : 2$ ;  $Y = 1.38$  gm. hydrogen.
- (c)  $45 : Z :: 65 : 161$ ;  $Z = 111.4$  gm. zinc sulphate.

Similar problems can be solved by this method.

### EXERCISES.

1. Define and illustrate the term *equivalent*. What is the equivalent of hydrogen, oxygen, sulphur, zinc, copper, magnesium, silver, potassium, aluminium?
2. What is the equivalent of chlorine and of bromine?
3. How are equivalents determined? Are they the result of theory or actual analysis?
4. Expand the topic, "Atomic weights are often multiples of equivalents."
5. What is the atomic weight of an element? How is it related to the equivalent weight of the element? Is an atomic weight absolute or relative? What is the standard of atomic weight?
6. What does O represent besides one atom of oxygen?
7. What is the approximate atomic weight of hydrogen, oxygen, and sodium?

### PROBLEMS.

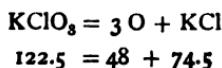
1. Calculate the percentage composition of (a) water ( $H_2O$ ), (b) zinc sulphide ( $ZnS$ ), (c) zinc carbonate ( $ZnCO_3$ ), (d) potassium chlorate ( $KClO_3$ ).
2. Calculate the percentage composition of (a) sugar ( $C_{12}H_{22}O_{11}$ ), (b) calcium sulphate ( $CaSO_4$ ), (c) zinc sulphate ( $ZnSO_4$ ), (d) magnesium oxide ( $MgO$ ), (e) copper oxide ( $CuO$ ).
3. Calculate the molecular weight of the following compounds by finding the sum of the atomic weights : (a) copper sulphate ( $CuSO_4$ ), (b) barium chloride ( $BaCl_2$ ), (c) manganese dioxide, (d) calcium oxide, (e) sodium hydroxide, (f) potassium hydroxide, (g) sodium carbonate, (h) potassium nitrate ( $KNO_3$ ).

4. Calculate the simplest formula of the compounds which have the indicated composition, and give the name of each compound: (a) H = 11.11, O = 88.89; (b) Na = 32.39, O = 45.07, S = 22.54; (c) C = 27.27, O = 72.72.

5. Calculate the simplest formula of the compounds which have the following composition: (a) N = 82.353, H = 17.647; (b) O = 30, Fe = 70; (c) H = 1, C = 11.99, O = 47.95, K = 39.06.

6. How much oxygen can be prepared from (a) 122.5 gm. of potassium chlorate, (b) 245 gm., and (c) 421 gm.?

Solution. The equation is—



These equation weights are obtained by adding the atomic weights found in the table. (a) By inspection, 122.5 gm. of potassium chlorate yield 48 gm. of oxygen. (b) The proportion needed is 122.5 : 48 :: 245 : x. And x = 96 gm. (c) Similarly, 122.5 : 48 :: 421 : x. And x = 164.9.

7. (a) How much oxygen can be prepared from 50 gm. of potassium chlorate, and (b) how much potassium chloride will remain?

$$\text{Ans. (a)} = 19.59, \text{(b)} = 30.41.$$

8. A certain weight of potassium chlorate was heated until completely decomposed. The residue weighed 20.246 gm. (a) What was its weight? (b) How much oxygen was evolved?  $\text{Ans. (a)} = 33.29, \text{(b)} 13.044$ .

9. What weight of potassium chlorate is needed to generate 144 gm. of oxygen?  $\text{Ans. } 367.5.$

10. What weight of potassium chloride remains after obtaining 8 gm. of oxygen from potassium chlorate?  $\text{Ans. } 12.416.$

11. How many grams of oxygen can be generated from 490 gm. of potassium chlorate?  $\text{Ans. } 192.$

12. How much hydrogen can be prepared from (a) 65 gm. of zinc, (b) 130 gm., (c) 297 gm.?  $\text{Ans. (c)} 9.14.$

13. How much zinc is needed to prepare (a) 2 gm. of hydrogen, (b) 14 gm., and (c) 17 gm.?

14. How much zinc sulphate can be prepared from (a) 98 gm. of sulphuric acid, (b) 196 gm., and (c) 427 gm.?  $\text{Ans. (c)} 701.5.$

15. A balloon holds 132.74 kg. of hydrogen. How much (a) zinc and (b) sulphuric acid are needed to produce the gas?

$$\text{Ans. (a)} 4314.05, \text{(b)} 6504.26.$$

16. How much (*a*) mercury and (*b*) oxygen can be obtained from 10 gm. of mercuric oxide? (Equation is  $HgO = Hg + O$ , or  $216 = 200 + 16$ .) *Ans.* (*a*) 9.259, (*b*) 0.74.

17. How much mercury will remain after obtaining 48 gm. of oxygen by heating mercuric oxide?

18. A lump of carbon weighing 24 gm. is burned in air. What weight of (*a*) carbon dioxide is formed and (*b*) oxygen is needed? (*c*) If a liter of oxygen weighs 1.43 gm., what volume of oxygen is needed? (Equation is  $C + O_2 = CO_2$ , or  $12 + 32 = 44$ .) *Ans.* (*c*) 44.75 l.

19. What weight of carbon dioxide is formed by burning 112 lb. of coal containing 15 per cent of impurities?

20. A lump of sulphur weighing 32 gm. is burned in air. Calculate the weight of (*a*) oxygen needed and (*b*) sulphur dioxide formed. (Equation is  $S + O_2 = SO_2$ , or  $32 + 32 = 64$ .)

21. Calculate the weight of oxygen needed to burn 731 gm. of sulphur containing 15 per cent of impurities. *Ans.* 621.35.

22. What weight of sulphur dioxide is formed by burning 67 per cent of 8794 kg. of sulphur?

23. Write the equations for the combination of sulphur and oxygen when they unite in the ratio (*a*) 1 : 1 and (*b*) 2 : 3. So also for carbon and oxygen in the ratio (*a*) 3 : 8 and (*b*) 3 : 4. Similarly for nitrogen and hydrogen in the ratio 4.66 : 1.

24. Write equations for the following reactions: (*a*) Magnesium and hydrochloric acid form magnesium chloride and hydrogen. (*b*) Sodium sulphate and barium chloride form barium sulphate and sodium chloride. (*c*) Calcium carbonate and hydrochloric acid form calcium chloride and carbon dioxide. (*d*) Lime (see index) and carbon dioxide form calcium carbonate. (*e*) Chlorine and phosphorus form phosphorus trichloride. (*f*) Carbon and copper oxide ( $CuO$ ) form copper and carbon dioxide.

## CHAPTER X.

### **LIGHT, HEAT, ELECTRICITY, AND CHEMICAL ACTION.**

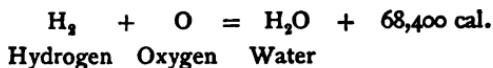
CHEMICAL action is always attended by one or more of the different forms of energy, such as light, heat, and electricity. This means that a chemical change involves not only a rearrangement of matter, but also a transformation of energy. Thus, when coal is burned, a new compound called carbon dioxide is formed, but heat is also liberated. Sometimes we pay more attention to the resulting matter than to the energy, but both are involved. In the present chapter we shall emphasize the relation of energy to chemical action. The law of the conservation of energy should be recalled in this connection. Energy, like matter, cannot be created or destroyed; we can only transform it. And the transformation involves no loss or gain. Hence, chemical energy, which is locked up, so to speak, in elements and compounds, reveals itself as heat, light, or electricity.

The Relation of Light to Chemical Action is illustrated in photography. Coatings consisting of compounds of silver and organic matter are quickly blackened by light (see Photography). Sunlight fades many colors. It likewise assists the chemical changes involved in the growth of plants. The formation of the green coloring matter of foliage is partly due to sunlight. A mixture of hydrogen and chlorine gases remains unchanged in the dark, but in direct sunlight it explodes violently. On the other hand, light is often a product of chemical action. Many chemical experiments show this, especially those with oxygen. Sparks, most flames, and the flash of a gun are other illustrations of the close relation between light and chemical action. Combustion in its varied forms is usually attended by light.

## HEAT AND CHEMICAL ACTION.

**Heat and Chemical Action** are closely related. A chemical change is almost invariably attended by the liberation or absorption of heat. Moreover, the heat involved can often be measured. Heat is measured in calories, a calorie being the quantity of heat necessary to raise the temperature of 1 gm. of water from 0° to 1° C. For example, the heat liberated by the burning of 1 gm. of hydrogen is 34,200 cal., and of 1 gm. of pure charcoal is about 8000 cal. Attention has already been called to the high temperature of the hydrogen flame (see Chapter III).

Ordinary chemical equations do not express changes in energy. To represent heat changes, the number of calories of heat involved is placed after the equation, thus : —



This is called a **thermal equation**, and it means that 68,400 cal. of heat are liberated when 2 gm. of hydrogen unite with 16 gm. of oxygen to form 18 gm. of water. In some changes heat disappears. Thus, when carbon unites with sulphur to form carbon disulphide, heat is absorbed. The equation expressing this fact is —



Heat involved in the formation of a particular compound is called **heat of formation** of that compound. If heat is liberated in the formation of a compound, the heat is called positive (+); and the compound is termed **exothermic**. Heat of formation which is absorbed is called negative (-); and a compound having a negative heat of formation is said to be **endothermic**. Exothermic compounds are stable, and can be decomposed only by the addition of the same quantity of heat liberated by their formation. Thus, 68,400 cal. of heat, or an equivalent quantity of energy, must be added to 18 gm. of water to decompose it

into 2 gm. of hydrogen and 16 gm. of oxygen. Such heat is called **heat of decomposition**. On the other hand, endothermic compounds are unstable, and often explosive. They decompose easily with the liberation of heat. Ozone is endothermic. Heat is absorbed during its formation from oxygen; but when ozone decomposes, heat is liberated. Two parts (by volume) of ozone form three parts (by volume) of oxygen and liberate 72,400 cal.

A familiar instance of the evolution of heat by chemical action is the slaking of lime. When lime and water are mixed, their union produces sufficient heat to boil water and often to set fire to wood. Steam can be seen escaping from the boxes in which lime is being mixed with water and sand to form plaster or mortar. Buildings in which lime is stored sometimes take fire, if rain leaks in upon the lime. Ships loaded with lime are in constant danger of being burned. Other substances liberate heat when added to water, *e.g.* sulphuric acid, sodium and potassium hydroxides, and the metals, sodium and potassium.

Heat is the initial cause of many chemical changes. It is necessary to start many reactions, just as a stone on top of a hill must be pushed before it will roll toward the bottom. Hydrogen and oxygen mix freely without combining, but union occurs the instant heat is applied in form of a flame or an electric spark. Similarly, illuminating gas must be lighted, *i.e.* raised to the **kindling temperature** before the chemical changes which cause the light and heat can proceed. These facts mean that chemical action often depends upon temperature. This statement has been strikingly illustrated in the last four years. At the extremely low temperature obtained by using liquid air and similar substances, it appears that many chemical reactions cease. While at the exceedingly high temperature produced by electricity many changes, chemical and physical, hitherto impossible, occur quickly and simply.

**The Electric Furnace.**—Until quite recently the intense heat needed for chemical changes was obtained by burning carbon or its compounds, such as charcoal, illuminating gas, and oil. Sometimes the blast lamp and oxyhydrogen blowpipe were used. But all these sources have been surpassed in efficiency by the electric furnace.

It is well known that an electric arc light produces intense heat. The high temperature of the arc, *i.e.* space between the glowing ends of the carbons, is unequaled by that of any other source of artificial heat. If the carbon rods are inclosed in a box that prevents the escape of heat, a temperature estimated to be about  $3500^{\circ}\text{C}$ . is produced inside the box. This apparatus is called an **electric furnace**. The French chemist, Moissan, was among the first to use the electric furnace in experimenting at high temperatures. One form of the electric furnace is shown in Figure 16.

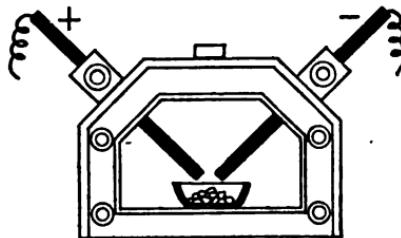


FIG. 16.—Electric furnace — arc type.

Moissan's description of his furnace is as follows: "It consisted of two bricks of quicklime placed one on top of the other. The lower brick contained a longitudinal groove to receive the two electrodes [carbon rods], and situated in the center was a small cavity. This cavity might vary in size, and contained a bed some centimeters in depth of the substance to be acted upon by the heat of the arc, or a small crucible of carbon containing the substance to be treated may be placed there. The upper brick was slightly hollowed out in the part just above the arc. As the intense heat of the current soon melted the



HENRI MOISSAN

1852-1907

1

surface of the lime, giving it, at the same time, a beautiful polish, a dome was obtained in this way which reflected all the heat on to the small cavity which contained the crucible."

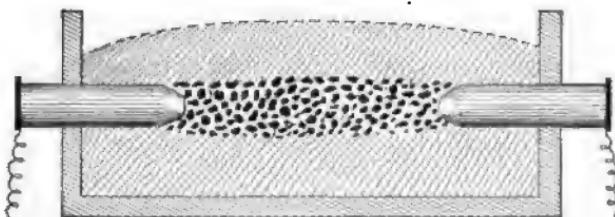


FIG. 17.—Electric furnace—resistance type.

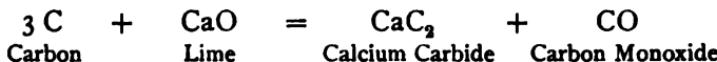
When a current is passed through the carbon rods, the tremendous heat produced is retained in the space by the non-conducting walls and acts upon the substance below the arc. The outside of the furnace remains cold enough to be touched by the hand, but the inside becomes very hot.

Another type of electric furnace is shown in Figure 17. In this kind the substance itself helps generate heat, for the electricity in passing from one electrode (as the carbon rods are called) through the substance to the other electrode meets with so much resistance that intense heat is produced.

In neither type of furnace is there any electrical action upon the chemicals. The intense heat alone produces the remarkable changes. Sand, lime, magnesium oxide, and other refractory oxides melt and volatilize. The elements carbon, silicon, and boron boil; and gold, copper, and platinum quickly melt and vaporize. Stable compounds of carbon, boron, and silicon are formed, called carbides, borides, and silicides. Some of the carbides have an industrial use as well as scientific interest, especially calcium carbide and silicon carbide (see below).

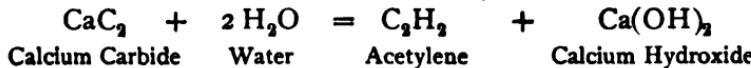
**Industrial Use of the Electric Furnace.**— Huge electric furnaces constructed on the resistance type are now in active operation. And since electricity is readily obtained in many localities by running dynamos by water, new industries requiring intense and continuous heat have recently sprung into existence. Several of these plants are located at Niagara Falls, which furnishes enormous power.

**Calcium Carbide** is made on a large scale by heating a mixture of lime and coke (a form of carbon) in an electric furnace. The chemical change is caused solely by the intense heat and may be represented thus:—



This method of making calcium carbide cheaply was discovered independently and at about the same time (1892–1895) by Moissan and Willson. The furnaces now in operation vary in details, but all have one essential feature, viz., the heat is generated by electricity passing through materials offering resistance. In most furnaces one electrode is a crucible wholly or partly of carbon, and the other electrode is a stout carbon pillar dipping into the mixture.

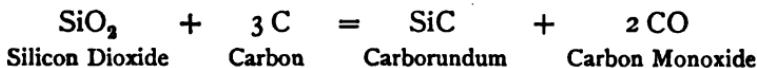
Calcium carbide is a hard, brittle, dark gray, crystalline solid with a metallic luster. Its specific gravity is 2.2. The most striking and useful property is its action with water, acetylene being formed, thus:—



Calcium carbide is used to generate acetylene gas. This gas burns with a brilliant flame, and is coming into general use as an illuminant. Owing to its action with water,

calcium carbide is packed and sold in air-tight cans (see Acetylene).

**Carborundum** is a compound of silicon and carbon, having the composition SiC. It is made in the electric furnace by fusing sand (silicon dioxide,  $\text{SiO}_2$ ), coke, sawdust, and common salt. The essential chemical change is represented thus:—



Carborundum is silicon carbide (or carbon silicide). It is a crystallized solid, varying in color from white to emerald green and is sometimes iridescent. It is extremely hard, being harder than ruby and nearly as hard as diamond. The extreme hardness of carborundum has led to its wide application as an abrasive, and large quantities are made into a great variety of grinding wheels, whetstones, and polishing cloths.

Carborundum is a good conductor of heat. Its specific gravity is about three. Acids have no action upon it, but it is decomposed by fusing with potassium hydroxide and other alkalies.

Carborundum is manufactured in a huge electric furnace, shown in Figure 18. It is an oblong box of bricks with permanent ends and loosely built sides. Each end is provided with a heavy metal plate. The wires for the electric current are attached to the outer ends of these plates, while the huge carbon electrodes fit into the inner ends, and project into the furnace. A cylinder of granulated coke makes an electrical connection between the electrodes. In this furnace the mixture is not heated by an electrical arc, but by the resistance of the carbon core to the passage of the powerful current of electricity. The chemical change, as in the manufacture of calcium carbide, is due solely to heat. The current is passed through the mixture for about eight hours. When the operation is over and the furnace is cool, the side walls are pulled down, and the carborundum is removed. The purest grade is found around the core. It is crushed, treated with sulphuric acid to remove the impurities, washed, dried, and graded according to the size of the particles.



FIG. 18.—Carborundum furnace in operation.

**Artificial Graphite** is now manufactured on a large scale at Niagara Falls by heating a special grade of coal or of coke in an electric furnace. The process is electro-thermal, and yields a product that is exceptionally suitable for the electrodes used in electrolytic and electrothermal apparatus. Graphite is a form of carbon.

## ELECTRICITY AND CHEMICAL ACTION.

**The Relation between Electricity and Chemical Action** has always been a fascinating subject. Volta constructed his voltaic pile about 1800. This was one of the first, perhaps the first, source of an electric current. In May, 1800, Nicholson and Carlisle decomposed water into hydrogen and oxygen by an electric current obtained from a thermopile. In the same year Cruikshank obtained lead and copper from solutions of their salts. And in 1807 Davy isolated the elements, sodium and potassium, by passing an electric current (obtained from a large battery) through fused caustic soda and caustic potash respectively. From that time until the present day, electrochemistry has been studied by chemists.

**Electricity is readily transformed into chemical energy, and vice versa.** A typical illustration of the transformation of chemical energy into electricity is furnished by the voltaic cell.

**The Voltaic (or Galvanic) Cell** in its simplest form consists of two metals connected by a wire and dipped into a liquid which will interact with one of the metals (Fig. 19). Copper, zinc, and water containing sulphuric acid may be used as an illustration. When the connected metals are put into the acid, the zinc slowly disappears and hydrogen bubbles appear on the copper. Further examination would show that the zinc and sulphuric acid interacted, forming zinc sulphate. The chemical change is the one already described under hydrogen, and may be represented thus :—

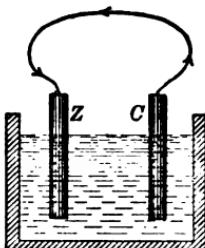
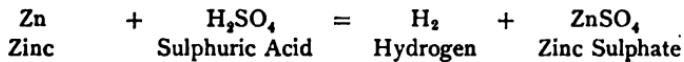


FIG. 19.—Voltaic cell.

The connecting wire becomes electrified and exhibits the effects of an electric current, viz., it becomes warm, it makes a magnetic needle move,

and a shower of sparks is produced if the wire is cut and one end is drawn down a file while the other is held firmly upon it. The source of the electric current is obviously the chemical action between the acid and zinc. The copper is necessary, otherwise the product of the chemical action would be merely heat. Carbon is often used in place of copper, and other liquids instead of sulphuric acid. The liquid chosen, however, must be one that will interact with zinc or its substitute. Several cells joined together form an **electric battery**. For many years the battery was the chief source of the electric current. And it is now used, especially for ringing telephone, house, fire alarm, and signal bells, and in operating the telegraph. The dynamo is now widely used to generate powerful currents of electricity.

**Electrochemical Terms.** — Faraday (1791–1867) investigated electrochemistry about 1834, and introduced many terms in common use. He called the decomposing process **electrolysis**, and the decomposable liquid the **electrolyte**; the wire by which the current entered he called the **anode**; and that by which it escaped, the **cathode**. “Finally,” he says, “I require a term to express those bodies which pass to the electrodes. I propose to distinguish such bodies by calling those anions which go to the anode of the decomposing body; and those passing to the cathode, cations; and when I have occasion to speak of these together, I shall call them ions. Thus, chloride of lead is an electrolyte, and when electrolyzed evolves the two ions, chlorine and lead, the former being an anion and the latter a cation.” These terms are used to-day, though in a somewhat broader sense. **Electrolysis** is the series of chemical changes accompanying the passage of an electric current through a dissolved or fused (*i.e.* melted) compound. The compound thus decomposed is an **electrolyte**. The metallic or carbon rods which conduct the current of electricity to and from the electrolyte are called the **poles**, or better, the **electrodes**. Electrodes are usually made of platinum, cop-

per, zinc, mercury, or hardened carbon ; they may have any shape — rod, wire, sheet, plate, box, crucible ; and they may also be solid, liquid, or powder, as well as fixed or movable. The electrodes are connected by wires with the source of the electric current, and serve as "doors" — to quote Faraday again — for the current to flow into and out of the electrolyte and through the wire connecting the electrodes. We speak of a "current" of electricity and of electricity as "flowing," although we do not know the nature of electricity, nor do we mean really that it flows, like a river, only in one direction. It is customary to speak of the current as entering the solution by the **anode** or **positive electrode** and leaving by the **negative electrode** or **cathode**. The anode is the electrode that is often consumed or worn away, either mechanically or chemically. But solids are often deposited upon the cathode, as will soon be described. **Ions** are the independent particles into which the electrolyte is decomposed ; they are charged with electricity. *Ion* comes from a Greek word which means wandering or migrating. And a **cation** is that ion which moves down or along with the current of electricity to the cathode, where it is separated, deposited, or modified ; while an **anion** is that ion which moves upward or against the current to the anode, where it likewise appears in various forms. Anions are electro-negative ions, but cations are electro-positive ions. Metallic ions are cations ; hence metals are deposited at the negative electrode or cathode. Non-metallic ions are usually anions, therefore oxygen, chlorine, and non-metallic groups (*e.g.* OH) appear at the anode. Hydrogen is electro-positive. In general, metals are electro-positive, and non-metals (except hydrogen) are electro-negative. Ions follow the law of electric attraction and repulsion : those charged with the same kind of electricity repel each

other, and those with unlike kinds attract. Hence the electro-positive cations move toward the electro-negative cathode, and the electro-negative anions move toward the electro-positive anode. Ions are further described under Ionization (see below). An **electrolytic cell** is the apparatus in which electrolysis takes place (Fig. 20). Its parts are analogous to the voltaic cell,—the containing vessel, the two electrodes, and the electrolytic solution. The vessel may have any desired shape, and is made of

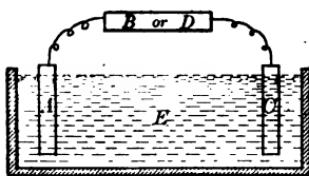


FIG. 20.—Electrolytic cell. *A* and *C* are the electrodes, *E* is the electrolyte, *B* or *D* is the battery or dynamo.

material which will resist the corrosive action of the electrolyte or which will withstand a high temperature. Unlike the voltaic cell, the electrolytic cell generates no electric current; it receives the current from a dynamo or a battery. Electrolysis is accomplished on a large scale in electrolytic cells.

**Illustrations of Electrolysis.**—Electrolysis may be simple, but it is usually very complex. Two illustrations will be given. When two platinum electrodes are put into hydrochloric acid and a current of electricity is passed, hydrogen is liberated at the cathode, and chlorine is liberated at the anode. This is a simple instance of electrolysis. But when an aqueous solution of sodium chloride is electrolyzed, the action is different. Theoretically, the products should be sodium and chlorine, but they are hydrogen, sodium hydroxide, and chlorine. The sodium liberated at the cathode immediately interacts with the water to form hydrogen and sodium hydroxide. Furthermore, unless the chlorine and sodium hydroxide are removed, they will interact to form compounds of chlorine, which vary in composition with the temperature, etc.

**Industrial Applications of Electrolysis.** — The earliest industrial application of electrolysis was in electrotyping and electroplating. These operations consist in depositing a thin film of metal upon a surface. They are fundamentally the same, though copper is the only metal used for producing electrotypes. **Electrotypes** are exact reproductions of the original objects. The process of **electrotyping** is substantially as follows: the page of type, or the woodcut, is first reproduced in wax or plaster. This exact impression is next covered with powdered graphite to make it conduct electricity. The coated mold is then suspended as the cathode in an acid solution of copper sulphate; the anode is a plate or bar of copper. When the current is passed, electrolysis occurs; copper is dissolved from the anode and deposited upon the mold in a film of any desired thickness. The exact copper copy is stripped from the mold, backed with metal or mounted on a wooden block, and used instead of the type or woodcut itself. By this process exact copies of expensive wood engravings can be cheaply reproduced, and type can be saved from the wear and tear of printing. Most books, magazines, and newspapers are now printed from electrotypes. The process of **electroplating** differs from electrotyping in only one essential, viz., in electroplating, the deposited film is not removed from the object. The object to be plated is carefully cleaned and made the cathode; the anode is a bar or plate of the metal to be deposited. When the current passes through the system, the metal is firmly deposited upon the object. The electrolysis would take place, of course, if any anode were present; but anodes of the metal to be deposited are usually used to prevent the solution or "bath" from weakening. They accomplish the purpose by replenishing the solution with metal

as fast as it is removed and deposited upon the cathode. Silver, nickel, and gold are the usual metals used in electroplating (see these metals).

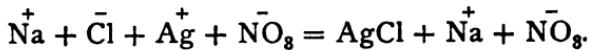
Electroplating and electrotyping have been done since about 1840. It is only within the last ten or fifteen years, however, that the electric current has been profitably applied in many industries. But during this time the development of electrochemistry has been very marked. The largest of these industries is the refining of copper. The process is similar to that described under electrotyping. Other metals, such as gold, silver, and lead, are extracted from their ores and purified by electricity, though the older processes are still used. All the aluminium, magnesium, and sodium of commerce are now manufactured by passing an electric current through their fused compounds. Nearly all the domestic potassium chlorate and much of the caustic soda are made by electrolysis. The same is true of barium compounds and many other chemicals. These electrochemical processes will be fully discussed in the appropriate places.

The Theory of Electrolytic Dissociation was first referred to briefly in discussing the nature of solution, again, more fully, in the chapter on Acids, Bases, and Salts, and a third time in the foregoing treatment of electrolysis. It is now appropriate to consider this theory at length. According to the theory, some of the molecules of certain substances called electrolytes (viz. acids, bases, and salts) dissociate in solution into electrically charged particles called ions; such solutions conduct electricity, and when the electric current passes, the charged particles or ions move to their proper electrodes, where various changes, both electrical and chemical, take place. Thus, when sodium chloride is dissolved in water, much of the salt dissociates

into the ions, sodium and chlorine; the sodium ions are charged positively, and the chlorine ions negatively. Now, when an electric current is passed into the solution, the ions move toward their proper electrodes. When the ions reach their respective electrodes, they give up their electric charges and assume their normal conditions. Thus, the positive sodium ions give up their charges at the negative electrode, or cathode, and become sodium atoms. The latter interact with water to form hydrogen and sodium hydroxide. Similarly, the negative chlorine ions give up their charges at the positive electrode, or anode, and become neutral atoms, which at once unite to form chlorine molecules.

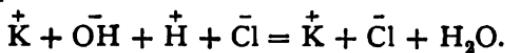
The dissociation of certain substances when in aqueous solution is also called **ionization**. Two kinds of ions are present in every electrolytic solution, viz. electro-positive ions, or **cations**, and electro-negative ions, or **anions**. Ions, although formed by the dissociation of molecules, are not identical with atoms, but differ mainly in having a charge of electricity. For example, when sodium chloride is dissolved in water, the electro-positive sodium ions move about in the water without producing any apparent chemical change; but ordinary sodium interacts violently with water, as we have already seen. Similarly, the chlorine ions circulate freely in water and exhibit none of the effects of gaseous chlorine upon water. In a word, in such a solution the sodium ions and chlorine ions exist side by side without any apparent decomposition of the water or any apparent tendency to combine with each other. It is customary to represent ions by chemical symbols supplemented by the sign which designates the kind of electric charge. Thus, the ions formed by the dissociation of sodium chloride are  $\text{Na}^+$  and  $\text{Cl}^-$ , while potassium nitrate yields  $\text{K}^+$  and  $\text{NO}_3^-$ .

**Application of the Theory of Electrolytic Dissociation.**—Many facts of chemistry become intelligible when interpreted by this theory. (1) **Ordinary tests are tests for ions.** For example, all chlorides in solution have the same test. That is, they all interact with silver nitrate in solution, because all have chlorine ions in the solution. Similarly, all soluble sulphates interact with barium chloride in solution, because all sulphates have  $\text{SO}_4^-$  ions in the solution. Both silver chloride and barium sulphate are insoluble, and are removed from the solution as precipitates. A complete illustration will make this fact clearer. The silver nitrate and sodium chloride solutions before mixing consist largely of the ions of silver,  $\text{NO}_3^-$ -group, sodium, and chlorine. When mixed, the ions of silver and chlorine unite to form silver chloride, which is insoluble and hence not ionized; the solution still contains ions of sodium and of the  $\text{NO}_3^-$ -group. On the other hand, if solutions of potassium chlorate and silver nitrate are mixed, no silver chloride is formed, because no chlorine ions are available. Potassium chlorate dissociates into ions of potassium and  $\text{ClO}_3^-$ . Equations are often used to express ionization. Thus, the **ionic equation** for the interaction of sodium chloride and silver nitrate is—



(2) **Ionization explains the General Properties of Acids, Bases, and Salts.** Acids in solution turn litmus red, because their solutions contain hydrogen ions ( $\text{H}^+$ ). Similarly, bases turn litmus blue, because their solutions contain hydroxyl ions ( $\text{OH}^-$ ). But solutions of neutral salts contain neither hydrogen nor hydroxyl ions, hence they do not affect litmus. The above principles can be readily

extended to cover acid and basic salts. The other general properties of acids and bases are believed to be due to the above causes. (3) **Neutralization**, interpreted by the ionic theory, is fundamentally the union of hydrogen and hydroxyl ions to form molecules of water. Suppose hydrochloric acid and potassium hydroxide are mixed. The solution at first contains the hydrogen, chlorine, potassium, and hydroxyl—all as ions. But the hydrogen and hydroxyl immediately unite to form water, leaving the potassium and chlorine ions in the solution. This solution is thus rendered neutral by the removal of the hydrogen ion—its acid constituent—and of the hydroxyl ion—its basic constituent. The ionic equation expressing the neutralization of potassium hydroxide by hydrochloric acid is—



The potassium and chlorine ions remain free and uncombined until the solution is evaporated. As the concentration increases, the ions unite until nothing remains except the neutral salt potassium chloride.

Neutralization, therefore, as interpreted by the ionic theory, is essentially a union of hydroxyl and hydrogen ions. This view is supported by much experimental evidence. For example, the **heat of neutralization** produced by the interaction of equivalent quantities of strong acids and bases is approximately the same, provided the solutions are dilute and other thermal changes do not occur. Thus, when 18 gm. of water are formed by the act of neutralization, 13,700 calories of heat are liberated. A general ionic equation for typical neutralization might be written—



Many cases of electrolysis are readily interpreted by the theory of electrolytic dissociation. The electrolysis of copper sulphate furnishes a typical illustration. The ions of a copper sulphate solution are copper ions ( $\text{Cu}^{++}$ ) and sulphate ions ( $\text{SO}_4^{- -}$ ). When this solution is electrolyzed, the copper ions ( $\text{Cu}^{++}$ ) migrate to the cathode, lose their elec-

tric charges, become copper atoms ( $\text{Cu}$ ), and adhere as metallic copper to the cathode. The sulphate ions ( $\text{SO}_4^{--}$ ) lose their electric charges at the anode and become ordinary uncharged atomic groups ( $\text{SO}_4$ ). But this group of atoms is chemically unstable, and immediately interacts with the water around the anode, forming sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and oxygen ( $\text{O}$ ). The oxygen escapes, but the sulphuric acid mingles with the solution and dissociates into its ions. Similarly, a solution of sodium sulphate when undergoing electrolysis yields sulphuric acid at the anode and sodium hydroxide ( $\text{NaOH}$ ) at the cathode; the electrolyte itself (sodium sulphate) furnishes directly only sodium and sulphate ions, which lose their charges at the electrodes, and by their subsequent chemical interaction with the water give the final result just stated. The so-called electrolysis of water is interpreted as follows: Water itself does not conduct electricity to an extent which is comparable with the behavior of an electrolytic solution, because water dissociates only inappreciably and gives therefore an exceedingly small number of ions. A solution of sulphuric acid contains hydrogen ions ( $\text{H}^+\text{H}^+$ ) and sulphate ions ( $\text{SO}_4^{--}$ ). When a current is passed through this solution, hydrogen ions migrate to the cathode, lose their electric charges, become hydrogen atoms, and eventually escape as hydrogen gas; the  $\text{SO}_4$ -ions migrate to the anode, lose their electric charges, become  $\text{SO}_4$ -groups, and interact with the water to form sulphuric acid and oxygen. The oxygen escapes as a gas, while the sulphuric acid dissociates into its ions. The water, therefore, is not split up directly into hydrogen and oxygen, as was formerly supposed. The two liberated gases are produced by the joint operations of electrolysis and subsequent chemical action, but the gases would not be liberated at all unless the ionization of the sulphuric acid had previously occurred in the solution.

**Degree of Dissociation of Acids, Bases, and Salts.**—The degree to which acids, bases, and salts dissociate is due to two factors, viz. the nature of the substance itself and the concentration of the solution. In general, dissociation is slight in a concentrated solution, and increases as the solution becomes more and more dilute. The percentage of dissociation of certain electrolytes in solutions of a definite strength and at the same temperature ( $18^\circ \text{ C.}$ ) is given in the following—

TABLE OF IONIZATION.

SUBSTANCE.	PER CENT OF IONIZATION.
Hydrochloric acid . . . . .	90
Nitric acid . . . . .	90
Sulphuric acid . . . . .	60
Potassium chloride . . . . .	85
Potassium nitrate . . . . .	83
Potassium hydroxide . . . . .	86
Sodium hydroxide . . . . .	86

Numerous facts support the theory of electrolytic dissociation. Only one, however, can be discussed here. It has long been known that solutions boil at a higher temperature and freeze at a lower temperature than pure water. A fresh-water river, for example, freezes before the ocean, and water containing considerable mineral matter boils at a higher temperature than pure drinking water. It is generally true that a dissolved substance *raises the boiling point and lowers the freezing point* of a given solution. Now, when weights of non-electrolytes equal to their molecular weights are dissolved in the same weight of water, the boiling point of each solution is raised the same number of degrees and the freezing point is lowered the same number of degrees. Thus, the freezing point of water is depressed about  $1.89^{\circ}$  C. by a solution of 342 gm. of cane sugar ( $C_{12}H_{22}O_{11}$ ) and 58 gm. of acetone ( $C_3H_6O$ ), each dissolved in 1000 gm. of water. But when solutions of electrolytes, *i.e.* acids, bases, and salts, are experimented with, the freezing point is lower than that produced by non-electrolytes under the same experimental conditions. Moreover, the depression is not uniform for all electrolytic solutions under uniform conditions. For example, a solu-

tion containing 58.5 gm. of sodium chloride to the liter depresses the freezing point of water about  $3.5^{\circ}$  C., or nearly twice the amount produced by a cane sugar solution of equivalent concentration. These facts lead us to believe that solutions of non-electrolytes contain only molecules, while solutions of electrolytes contain ions into which some of the molecules have dissociated. Hence the number of independent particles (molecules and ions) in the electrolytic solution is greater than in the non-electrolytic solution. Ions and molecules act alike on the freezing point of a solution, and the larger the number of particles, the greater the depression. Analogous statements can be made about the elevation of the boiling point of solutions.

#### EXERCISES.

1. What transformations of energy accompany chemical action? Illustrate your answer.
2. State and illustrate the law of the conservation of energy.
3. Discuss the relation of light to chemical action. Give popular and scientific illustrations of (a) the production of chemical action by light, and (b) production of light by chemical action.
4. Define and illustrate (a) calorie, (b) thermal equation, (c) heat of formation, (d) exothermic, (e) heat of decomposition, (f) endothermic, (g) negative heat.
5. Give several illustrations of the production of (a) heat by chemical action, and (b) *vice versa*.
6. When an electric spark is passed through a mixture of two volumes of hydrogen and one volume of oxygen, what is the result? Is it due directly to electricity or to heat?
7. Define and illustrate kindling temperature.
8. Name several sources of heat. How may electricity be used as a source of heat?
9. Describe Moissan's electric furnace. Why is it so efficient? Is its effect thermal or electrical? State some results produced by Moissan with this furnace. Describe both types of electric furnace. Has the electric furnace any industrial use? Where?

10. What is calcium carbide? How is it made? State the equation for the reaction. What are its properties? For what is it used? How should it be stored?
11. What is carborundum? How is it made? State the equation for the reaction. What are its properties and uses?
12. What is artificial graphite? How is it made? For what is it used?
13. Give several illustrations of the production of (*a*) electricity by chemical action, and (*b*) *vice versa*.
14. State briefly the first chemical changes which were produced by electricity.
15. Describe a simple voltaic cell. Why is it so called? What is the source of the electric current manifested by the cell? What is an electric battery? For what is it used?
16. Define and illustrate (*a*) electrolysis, (*b*) electrolyte, (*c*) electrode, (*d*) anode, (*e*) cathode, (*f*) ions, (*g*) anion, (*h*) cation, (*i*) positive electrode, (*j*) negative electrode, (*k*) ionization, (*l*) electrolytic dissociation.
17. Where are (*a*) anions and (*b*) cations liberated?
18. Describe an electrolytic cell. How does it differ from a voltaic cell? For what is it used?
19. Describe the electrolysis of (*a*) hydrochloric acid, (*b*) sodium chloride, (*c*) water.
20. Compare acids, bases, and salts as to relative ionization in solutions of the same concentration.
21. Give a brief account of Faraday's contribution to electrochemistry.
22. Describe the process of (*a*) electrotyping and (*b*) electroplating.
23. State some industrial applications of the electric current.
24. What is the theory of electrolysis? What is the present theory of solution in water? What is the theory called? Why? What facts support it?
25. Define and illustrate an ionic equation. Write the ionic equation for the interaction of nitric acid and potassium hydroxide.
26. Write equations for the following: (*a*) Iron and sulphur combine in the ratio of 7 to 4. (*b*) Ammonia gas and hydrochloric acid gas form ammonium chloride.

## PROBLEMS.

1. Calculate the percentage composition of (a) water, (b) magnetic oxide of iron ( $\text{Fe}_3\text{O}_4$ ), (c) crystallized sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ).
2. If a certain current of electricity deposited 31.7 gm. of copper, how much (a) silver, (b) aluminium, and (c) magnesium would it deposit?
3. If a certain current of electricity deposited 2 kg. of copper, how much silver would it deposit?
4. How much calcium carbide can be made (theoretically) from a ton of lime? (Equation is  $3\text{C} + \text{CaO} = \text{CaC}_2 + \text{CO}$  or  $36 + 56 = 64 + 28$ .)
5. How much carborundum can be made (theoretically) from a ton of sand ( $\text{SiO}_2$ )? (Equation is  $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$  or  $60 + 36 = 40 + 56$ .)
6. Calculate the percentage composition of (a) carborundum and (b) calcium carbide.

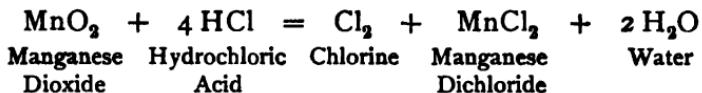
## CHAPTER XI.

### CHLORINE AND HYDROCHLORIC ACID.

CHLORINE is an important element, and its compounds are useful, especially hydrochloric acid, sodium chloride, and bleaching powder.

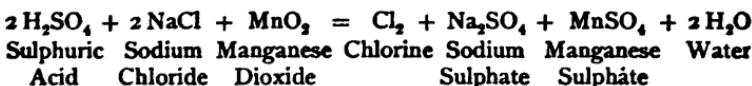
**Occurrence.**—Free chlorine is never found in nature, because it combines so readily with other elements. But in combination it is widely distributed, since it is one of the components of common salt, or sodium chloride. Many compounds of chlorine with potassium, magnesium, and calcium are found in the deposits at Stassfurt in Germany (see these metals). The salts found in sea water contain about 55 per cent, and the earth's crust contains about 0.01 per cent of chlorine. Silver chloride—"horn" silver—is mined as an ore in the United States and Mexico.

**Preparation.**—Chlorine is prepared in the laboratory by heating a mixture of manganese dioxide and hydrochloric acid. This method was used by Scheele, who discovered the gas in 1774. The equation for the preparation of chlorine is—



This is an oxidizing process, since the hydrogen of the hydrochloric acid is oxidized to water, although only part of the chlorine of the acid is obtained free.

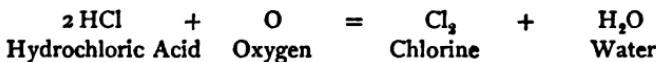
Sometimes chlorine is prepared in the laboratory by heating a mixture of manganese dioxide, sodium chloride, and sulphuric acid. This method is substantially the same as the other, since a mixture of sulphuric acid and sodium chloride yields hydrochloric acid. The simplest equation for this method of preparing chlorine is —



Other oxidizing substances besides manganese dioxide may be used, such as potassium chlorate ( $KClO_3$ ), potassium dichromate ( $K_2Cr_2O_7$ ), and red lead ( $Pb_2O_3$ ).

Chlorine is manufactured by several processes, all of which involve the same principle as the laboratory method.

In the Deacon process, hydrochloric acid is oxidized by oxygen obtained from the atmosphere. A mixture of hydrochloric acid gas and air is heated to 500° C. and passed through iron tubes containing balls of clay or pieces of brick previously saturated with copper chloride. A series of complex reactions occurs which are not well understood. It is supposed that the copper chloride facilitates the formation of chlorine by continuously giving and taking this gas. The essential chemical change, however, is the oxidation of the hydrochloric acid, and it may be represented by the equation —



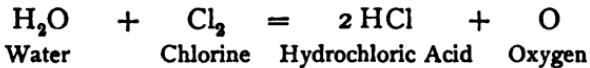
In the Weldon process, an impure native manganese dioxide, known as pyrolusite, is treated with hydrochloric acid in large earthenware retorts or stone tanks heated by hot water or steam. When no more chlorine is liberated, the residue is mainly manganese dichloride. This "still-liquor" was formerly thrown away, but by the Weldon process it is changed into manganese compounds, which are used to prepare more chlorine (see Manganese Dioxide).

Chlorine is also prepared on a large scale by the **electrolytic process**. Sodium chloride is decomposed by electricity in properly constructed cells, and the chlorine which is liberated at the anode is conducted off through pipes to the bleaching powder factory. Sodium hydroxide is produced at the same time, and the process will be described under this compound.

**Properties.**—Chlorine is a greenish yellow gas. Its color suggested the name chlorine (from the Greek word *chloros*, meaning greenish yellow), which was given to it by Davy about 1810. It has a disagreeable, suffocating odor, which is very penetrating. If breathed, it irritates the sensitive lining of the nose and throat, and a large quantity would doubtless cause death. It is heavier than the other elementary gases, and is about 2.5 times heavier than air. Hence it is easily collected by downward displacement, *i.e.* by allowing it to fall to the bottom of a bottle and thus fill the latter by displacing the air.

A liter of dry chlorine at  $0^{\circ}$  C. and 760 mm. weighs 3.22 gm.

Water dissolves chlorine. The solution is yellowish, smells strongly of chlorine, and is frequently used in the laboratory as a substitute for the gas. **Chlorine water**, as the solution is called, is unstable even under ordinary conditions, and must be kept in the dark. If the solution is placed in the sunlight, oxygen is soon liberated and hydrochloric acid is formed. Intermediate changes doubtless occur; but the simplest equation for the essential change is—



Chlorine is much less soluble in a solution of sodium chloride, over which it is sometimes collected. It attacks mercury and cannot be collected over this liquid.

Chlorine does not burn in the air, but many substances burn in chlorine. The metals antimony and arsenic, when sprinkled into chlorine, suddenly burst into flame, while phosphorus melts at first and finally burns with a feeble flame. If sodium, iron powder, brass wire, or other metals are heated and then put into chlorine, they burn; the sodium and iron produce a dazzling light and the brass

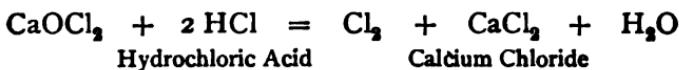
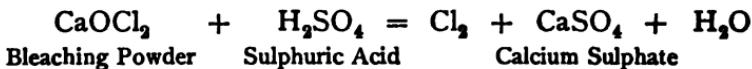
glows and emits dense fumes of whitish smoke. Chlorine combines readily with hydrogen. Hence, a jet of burning hydrogen when lowered into chlorine continues to burn, forming hydrochloric acid gas, which appears as a white cloud. The simplest equation for this change is—



The attraction between chlorine and hydrogen is so great that many compounds of hydrogen are decomposed by chlorine. Thus, compounds containing hydrogen and carbon, such as illuminating gas, paraffin wax, and wood, burn in chlorine with a smoky flame. Chlorine does not combine directly with carbon, hence the flame consists largely of very fine particles of solid carbon. Similarly, a piece of glowing charcoal is extinguished by chlorine. If filter paper is saturated with warm turpentine (a compound of hydrogen and carbon) and put into a bottle of chlorine, a flame accompanied by a dense cloud of black smoke bursts from the bottle ; the chlorine withdraws the hydrogen to form hydrochloric acid, while the carbon is left free.

The power to bleach is the most striking and useful property of chlorine. This property depends upon the fact, already mentioned, that chlorine withdraws hydrogen and liberates free oxygen ; the latter then decomposes the coloring matter in the cloth or other material. Dry chlorine does not bleach. If an envelope on which the postmark, or a lead pencil mark, is still visible is placed in moist chlorine, these marks will not be bleached because they are largely carbon ; but the writing ink, which is mainly a compound of hydrogen, carbon, and iron, will disappear. Litmus paper and calico are both bleached by moist chlorine.

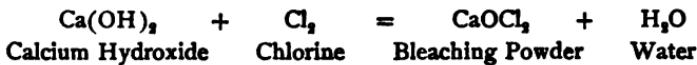
**Bleaching Powder** is the source of the chlorine used in the bleaching industries. It is sometimes called "bleach," or "chloride of lime." It is a yellowish white substance having a peculiar odor, which resembles that of chlorine. When dry, it is a powder, but on exposure to the air, it absorbs water and carbon dioxide, becomes lumpy and pasty, and loses some of its chlorine. Acids like sulphuric and hydrochloric acid liberate from bleaching powder its "available chlorine," which varies from 30 to 38 per cent in good qualities. The equations for the interaction of acids and bleaching powder are usually written thus —



The composition of bleaching powder has been much discussed. The most reliable authority gives it the formula  $\text{CaOCl}_2$ . When dissolved in water, bleaching powder forms calcium hypochlorite ( $\text{CaO}_2\text{Cl}_2$ ) and calcium chloride ( $\text{CaCl}_2$ ).

**Bleaching Powder** is manufactured by the action of chlorine gas on lime. Lime (calcium oxide,  $\text{CaO}$ ) is carefully slaked with water to form calcium hydroxide ( $\text{Ca(OH)}_2$ ). This powder is sifted into a large absorption chamber made of iron, lead, or tarred brick until the floor is covered with a layer three or four inches deep. The chlorine enters at the top and settles slowly to the floor, where it is absorbed by the lime.

The simplest equation for the formation of bleaching powder might be written —



**Bleaching.** — Immense quantities of bleaching powder are used to whiten cotton and linen goods and paper pulp. The pieces of cotton cloth as they come from the mill are

sewed end to end in strips, which are stamped at the extreme ends with some indelible mark to distinguish each owner's cloth. These strips, which are often several miles long, are drawn by machinery into and out of numerous vats of liquors and water, between rollers, and through machines, until they are snow-white and ready to be finished (*i.e.* starched and ironed) or dyed. The whole operation requires three or four days.

The preliminary treatment consists in singeing off the downy pile and loose threads by drawing the cloth over hot copper plates or through a series of gas flames. The object of the remaining operations is threefold, (1) to wash out mechanical impurities, the fatty and resinous matter, and the excess of the different chemicals, (2) to remove matter insoluble in water, and (3) to oxidize the coloring matter by chlorine. The details of the process differ with the texture of the cloth and with its ultimate use. The threefold object above mentioned involves successively "liming," "souring," "chemicking," and "souring," interspersed with frequent washing. The "liming" consists in boiling the cloth in a large kier or vat with lime, the "souring" in wetting it with weak sulphuric or hydrochloric acid, and the "chemicking" in impregnating it with a weak solution of bleaching powder. Often the cloth is boiled at a certain stage with resin and sodium carbonate. The "liming" removes the resinous and the fatty matter, the first "souring" neutralizes traces of lime, and the second, which follows the "chemicking," liberates the chlorine in the fiber of the cloth. Frequent washing is absolutely necessary to remove the impure products of the chemical changes as well as the excess of lime and other alkali, acid, and chlorine. Should these be left, the cloth would be unevenly bleached and its fiber would be weak. The cloth is finally treated with an *antichlor*, such as sodium hyposulphite, which removes the last traces of chlorine.

Bleaching is chemically an oxidizing process. The oxygen when it is liberated from water by chlorine is said to be in the **nascent state**. This means that the gas is exceedingly active, because it is not only uncombined, but just ready to unite with those elements for which it has great affinity. Hence this nascent oxygen literally tears

down complex colored substances and changes them into colorless compounds. The nascent state is aptly illustrated by bleaching because both the chlorine and the oxygen are in this active chemical condition.

**Chlorine Hydrate** is formed by cooling chlorine water or by passing chlorine into ice water. It is a yellowish, crystalline solid, and in the air it decomposes quickly into chlorine and water. Its composition corresponds to the formula  $\text{Cl}_2 \cdot 8 \text{ H}_2\text{O}$ .

**Liquid Chlorine** was first prepared by Faraday in 1823. A little chlorine hydrate was inclosed in one arm of a bent tube (Fig. 21), which was then sealed. By gently heating the tube, the chlorine hydrate was decomposed into chlorine and water, but the chlorine, being unable to escape, was condensed to a liquid by the pressure inside the tube. The liquefaction is more easily accomplished if one end is kept cold during the experiment.

At the ordinary pressure, chlorine gas becomes liquefied, if its temperature is  $-34^\circ\text{C}.$ , while at a pressure of six atmospheres the temperature need be only  $0^\circ\text{C}$ . Liquid chlorine has a bright yellow color. It is a commercial article, and is stored and shipped in steel cylinders lined with lead. It is used in the laboratory to prepare chlorides, and industrially to extract gold. Solid chlorine has been obtained as a yellow crystalline mass by cooling the liquid to  $-102^\circ\text{C}$ .

**Uses of Chlorine.**—Chlorine is used directly to prepare some of its compounds, the most important being bleaching powder. The latter is often used as a deodorizer and disinfectant, since the liberated chlorine destroys putrefying matter by acting on it as on coloring matter. A solution of potassium hypochlorite (Javelle's water) or sodium hypochlorite (Labarraque's solution) is often used to remove fruit stains from cotton and linen goods.

**Chlorides** are formed when chlorine combines with other elements, and they are in general stable compounds.

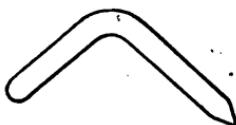
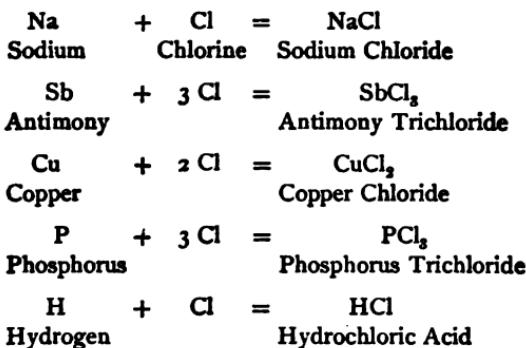


FIG. 21.—Bent tube for the liquefaction of chlorine.

The simplest equations illustrating the combination of chlorine with metals and other elements are —



Chlorides form an important class of compounds and they will be considered under the elements with which the chlorine combines. (See also Chlorides below.)

#### HYDROCHLORIC ACID.

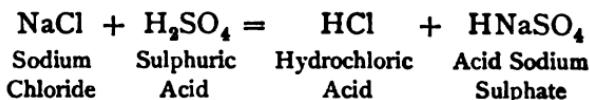
**Hydrochloric Acid** is the most useful compound of chlorine. It is a gas, very soluble in water. This solution has long been known as **muriatic acid** (from the Latin word *muria*, meaning brine). The term *hydrochloric acid* includes both the gas and its solution, but the solution is usually meant.

The early chemists called the gas "spirit of salt." Priestley, who first prepared, collected, and studied the gas, called it "marine acid air." Both expressions emphasize its relation to salt (sodium chloride).

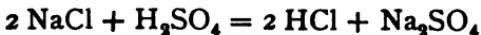
**Occurrence.** — The gas occurs free in volcanic gases. The solution is one constituent of the gastric juice of the stomach. Chlorides, which are salts of hydrochloric acid, are abundant in the earth's crust.

**Preparation.** — The gas is prepared in the laboratory by the method devised by Glauber in the seventeenth cen-

tury, viz., by heating sulphuric acid and sodium chloride. If the mixture is gently heated, the chemical change is represented thus —



But at a high temperature the equation for the reaction is —



In either case the gas is readily produced. It may be collected over mercury or, more easily, by downward displacement. The solution is prepared by passing the gas into water.

That sodium sulphate is the other product of the chemical change at a high temperature may be shown by testing the heated residue as follows: (a) Dissolve a portion in water and add a few drops of barium chloride solution; the immediate formation of the white, insoluble barium sulphate shows that the residue from the experiment must be a sulphate. (b) Burn a little of the residue on a platinum wire or piece of porcelain held in the Bunsen flame; the intense yellow color immediately imparted to the flame shows that the residue contains sodium. (c) Hence the compound must be sodium sulphate.

**Commercial Hydrochloric Acid** is manufactured in enormous quantities by the method used in the laboratory. A mixture of salt and sulphuric acid is moderately heated in a large hemispherical cast-iron pan, and the gas passes through an earthenware pipe into an absorbing tower; the fused mass of acid sodium sulphate and salt is then subjected to a higher temperature, and the liberated gas passes by another pipe into the absorbing tower. These towers are tall and filled with coke or pieces of brick over which water trickles; as the hydrochloric acid gas passes up the tower, it is absorbed by the descending water, and flows

out at the bottom of the tower as concentrated acid. The gas is usually cooled before it enters the towers. Sometimes the gas passes through huge earthenware jars before entering the towers. In these jars the gas and water are caused to flow constantly in opposite directions, thus insuring complete absorption.

Hydrochloric acid gas is a by-product in the manufacture of sodium carbonate by the Leblanc process. The gas was formerly allowed to escape into the atmosphere, but since it destroyed vegetation and became a nuisance in other ways, a law was passed forbidding the manufacturers to let it escape. Hence it became necessary to absorb the gas in water. The hydrochloric acid, which was once regarded as a waste product, is now the main source of profit, since competition has reduced the price of sodium carbonate (see Sodium Carbonate).

**Properties.** — Hydrochloric acid gas is colorless and transparent. When it escapes into moist air, it forms fumes which are really minute drops of a solution of the gas in the moisture of the air. It has a choking, sharp, pungent odor. The gas does not burn nor support combustion. It is about 1.25 times heavier than air, and may therefore be collected by downward displacement.

One liter at  $0^{\circ}\text{C}$ . and 760 mm. weighs 1.64 gm. The gas can be liquefied at  $10^{\circ}\text{C}$ . and 40 atmospheres pressure; while at  $-16^{\circ}\text{C}$ ., the pressure need be only 20 atmospheres.

The extreme solubility of hydrochloric acid gas in water is one of its most striking properties. One liter of water will dissolve about 500 l. of gas, if both are at  $0^{\circ}\text{C}$ . and 760 mm. At the ordinary temperature about 450 l. of gas dissolve in 1 l. of water, and as the temperature rises the solubility decreases. The solution is the familiar hydrochloric acid. The gas readily escapes, hence the acid forms fumes when exposed to air. Pure hydrochloric acid is a colorless liquid. The commercial acid has a yellow color, usually due to iron

compounds, but sometimes to organic matter or to dissolved chlorine. It also contains other impurities. Like most acids, it reddens blue litmus, and gives up its hydrogen when added to metals.

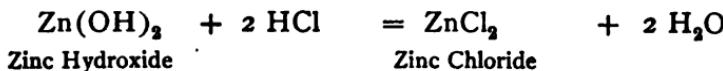
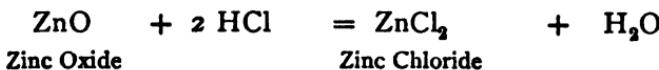
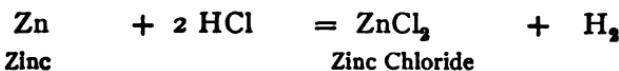
The strongest acid contains about 42 per cent (by weight) of the gas, and its specific gravity is 1.2. When the strong acid is heated, the gas is evolved until the solution contains about 20 per cent of the acid, and then the liquid boils at 110° C. without further change. The dilute acid, on the other hand, loses water until the same conditions prevail.

**Composition of Hydrochloric Acid Gas.** — In 1810, Davy showed that hydrochloric acid gas (which had been regarded as an oxygen compound) contained only chlorine and hydrogen. Many facts lead us to conclude that hydrochloric acid gas is composed of hydrogen and chlorine in such a ratio that its composition is represented by the formula HCl. (1) Hydrogen burns in chlorine, and the only product is hydrochloric acid gas. (2) When hydrochloric acid is decomposed by an electric current, equal volumes of hydrogen and chlorine are evolved. (3) When a mixture of equal volumes of hydrogen and chlorine is exposed to the direct sunlight or to the action of an electric spark, the gases combine with an explosion, and hydrochloric acid gas is formed with no residue. Furthermore, the volume of the resulting gas equals the sum of the volumes of hydrogen and chlorine used. (4) When a given volume of dry hydrochloric acid gas is treated with sodium amalgam, the chlorine is withdrawn by the sodium in the amalgam, and a volume of hydrogen remains which is half the original volume. (5) No derivative of hydrochloric acid is known which contains less hydrogen or less chlorine in a molecule. (6) The ratio by weight in which hydrogen and chlorine combine is 1 : 35.45. Hence, the lowest molecular weight of hydrochloric acid is 36.45, a number which has been verified by several different methods.

**Uses of Hydrochloric Acid.** — Vast quantities are used to prepare chlorine for the manufacture of bleaching powder. Various chlorides are prepared from it, and it is one of the common acids used in chemical laboratories.

**Chlorides** are formed by the direct addition of chlorine to metals, as we have seen. They are also formed when

metals, their oxides, or hydroxides are added to hydrochloric acid. The following equations illustrate this general fact :—



They are also formed by adding other salts to hydrochloric acid.

Molecules of chlorides may contain several atoms of chlorine. Occasionally the name of the compound indicates this fact, e.g. manganese dichloride ( $\text{MnCl}_2$ ), antimony trichloride ( $\text{SbCl}_3$ ), phosphorus trichloride and pentachloride ( $\text{PCl}_3$  and  $\text{PCl}_5$ ). If a metal forms two chlorides, the two are distinguished by modifying the name of the metal. The one containing the smaller proportion of chlorine ends in -ous, the one containing the larger ends in -ic. Thus, mercurous chloride is  $\text{HgCl}$ , but  $\text{HgCl}_2$  is mercuric chloride. Similarly, we have ferrous chloride,  $\text{FeCl}_2$ , and ferric chloride,  $\text{FeCl}_3$ .

**The Test for Hydrochloric Acid and Chlorides.** — Most chlorides are soluble in water. Those of lead, silver, and mercury (-ous) are not. If silver nitrate is added to hydrochloric acid, or to the solution of a chloride, a white, curdy precipitate of silver chloride is formed, which (*a*) is insoluble in nitric acid, but soluble in warm ammonium hydroxide, and (*b*) turns purple in the sunlight. The invariable formation of silver chloride is the **test for hydrochloric acid and soluble chlorides**. Hydrochloric acid gas also forms dense white clouds of ammonium chloride in the presence of ammonia gas. The usual test, viz. the pre-

cipitation of silver chloride, is applicable to both hydrochloric acid and a chloride, because both yield chlorine ions ( $\text{Cl}^-$ ). (See page 126.)

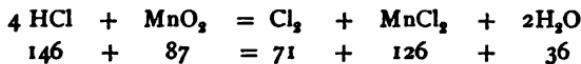
### EXERCISES.

1. What is the symbol of chlorine? What useful compounds contain this element?
2. How is chlorine prepared in the laboratory? Give one equation for its preparation. Describe Deacon's process for manufacturing chlorine.
3. Who discovered chlorine? Who named it, when, and why?
4. Summarize the physical properties of chlorine. How can it be quickly distinguished from the gases previously studied?
5. Summarize the chemical properties of chlorine. Compare it with oxygen. Describe fully its action with hydrogen.
6. Define (a) downward displacement, (b) available chlorine, (c) antichlor.
7. Develop the topics: (a) nascent state, (b) chlorine water, (c) chlorine hydrate, (d) liquid chlorine, (e) chlorine is an oxidizing agent.
8. What is bleaching powder? How is it made? What are its chief properties? Describe the operation of bleaching. What is the chemistry of bleaching?
9. What is (a) "bleach," (b) muriatic acid, (c) chloride of lime, (d) "salt," (e) "lime," (f) commercial hydrochloric acid?
10. What are chlorides? Name five. How can they be formed? Give the formula of sodium chloride. Why cannot chlorine be collected over mercury?
11. What is hydrochloric acid? How is it prepared in the laboratory? Give the equations for its preparation. How is it prepared industrially?
12. Summarize the chief properties of hydrochloric acid gas. Of the acid, as the term is usually used. What happens when hydrochloric acid is boiled?
13. What is the evidence that the formula of hydrochloric acid gas is  $\text{HCl}$ ?
14. For what is hydrochloric acid used? State the test for hydrochloric acid and soluble chlorides.

15. Give a brief account of Faraday's work on chlorine. Of Davy's work.  
 16. Why is chlorine never found free?

### PROBLEMS.

1. One equation for the preparation of chlorine is—



(a) How many grams of chlorine can be made from 247 gm. of manganese dioxide? (b) Name all the products.

2. How much sodium chloride is needed to prepare a kilogram of hydrochloric acid gas?

3. How many grams of manganese dioxide are necessary to prepare 100 gm. of chlorine from hydrochloric acid.

4. A bottle of chlorine water was exposed to the sunlight until all the chlorine disappeared. (a) What two products were formed? (b) Write the equation for the reaction. (c) What weight of chlorine gas is necessary to form 20 gm. of the gaseous product? (d) What volume of chlorine is necessary to form 20 gm. of the other product?

5. Calculate the percentage composition of (a) hydrochloric acid gas, (b) sodium chloride, (c) silver chloride ( $\text{AgCl}$ ), (d) potassium chloride ( $\text{KCl}$ ).

## CHAPTER XII.

### COMPOUNDS OF NITROGEN.

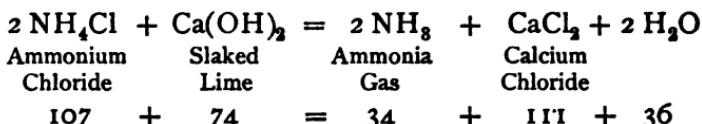
THE most important compounds of nitrogen are ammonia ( $\text{NH}_3$ ), nitric acid ( $\text{HNO}_3$ ), and compounds related to them. Many animal and vegetable substances essential to life are compounds of nitrogen.

#### AMMONIA.

The term ammonia includes both the gas and its solution in water, though the latter is more accurately called ammonium hydroxide.

**Formation of Ammonia.** — When vegetable and animal matter containing nitrogen decays, the nitrogen and hydrogen are liberated in combination, as ammonia. The odor of ammonia is often noticed near stables. If animal substances containing nitrogen are heated, ammonia is given off. The old custom of preparing ammonia by heating horns and hoofs in a closed vessel, *i.e.* by dry distillation, gave rise to the term "spirits of hartshorn." Soft coal contains compounds of nitrogen and of hydrogen, and when the coal is heated to make illuminating gas, one of the products is ammonia.

**Preparation.** — Ammonia gas is prepared in the laboratory by heating ammonium chloride with an alkali, usually slaked lime. The reaction may be represented thus —



The gas is usually collected by upward displacement, *i.e.* by allowing the gas to flow upward into a bottle and displace the air. The solution is prepared by conducting the gas into water.

The main source of the **ammonia of commerce** is the ammoniacal liquor or gas liquor of the gas works. The gases which come from the retorts in which the coal is heated are passed into water, which absorbs the ammonia and some other gases. This impure gas liquor is treated with lime to liberate the ammonia, which is absorbed in tanks containing hydrochloric acid or sulphuric acid. This solution upon the addition of an alkali gives up its ammonia, which is dissolved in distilled water, forming thereby the **ammonium hydroxide** or **aqua ammonia** of commerce.

Ammonia is sometimes prepared from the residues of the beet sugar industry, from the refuse of slaughter houses and tanneries, and from the gases from coke ovens. It is not obtained directly from the nitrogen of the air.

**Properties of Ammonia.** — Ammonia gas is colorless. It has an exceedingly pungent odor, and if inhaled suddenly or in large quantities it brings tears to the eyes and may cause suffocation. It is a light, volatile gas, being only .59 times as heavy as air. A liter of the gas at  $0^{\circ}$  and 760 mm. weighs .77 gm. It will not burn in the air, nor will it support the combustion of a blazing stick ; but if the air is heated or if its proportion of oxygen is increased, a jet of ammonia gas will burn in it with a yellowish flame, thereby illustrating the broader application of the term *combustion*.

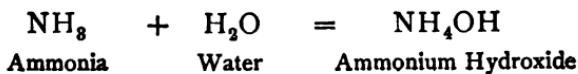
Ammonia gas is easily liquefied if reduced to  $0^{\circ}\text{C}$ . and subjected to a pressure of 4.2 atmospheres, while at  $-34^{\circ}\text{C}$ . it liquefies at the ordinary atmospheric pressure.

**Liquefied ammonia** is often called **anhydrous ammonia**, because it contains no water. It boils at  $-33.5^{\circ}\text{C}$ . Hence, if it is exposed to the air or warmed in any way, it changes back to a gas, and in so doing absorbs considerable heat. This fact has led to the extensive use of **liquid ammonia** in the manufacture of ice.

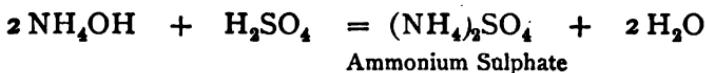
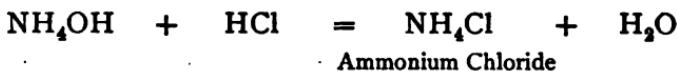
Ammonia is a common alkali, and was called formerly the **volatile alkali**. Priestley, who discovered and studied the gas, called it **alkaline air**.

Another marked property of ammonia gas is its solubility in water. A liter of water at  $0^{\circ}\text{C}$ . dissolves 1148 l. of gas (measured at  $0^{\circ}\text{C}$ . and 760 mm.), and at the ordinary temperature 1 l. of water dissolves about 700 l. of gas. This solution of the gas is usually called ammonia, though other names, especially ammonium hydroxide, are sometimes applied to it. Commercially it is known as **aqua ammonia**, ammonia, or ammonia water. It gives off the gas freely, when heated, as may easily be discovered by the odor or by the formation of the dense white fumes of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) when the solution is exposed to hydrochloric acid. The solution is lighter than water, its specific gravity being about .88, and contains about 35 per cent (by weight) of the gas. Ammonium hydroxide has an alkaline reaction, neutralizes acids and forms salts, and acts in many respects like sodium hydroxide.

**Ammonium Hydroxide and Ammonium Compounds.**—When ammonia gas is passed into water, it is believed that the ammonia combines with the water and forms a solution of an unstable compound having the formula  $\text{NH}_4\text{OH}$ . This compound is **ammonium hydroxide** (or ammonium hydrate). Its formation may be represented thus —



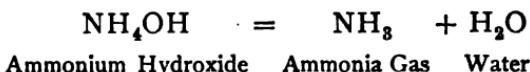
Ammonium hydroxide acts like a base. It has a marked alkaline reaction; it neutralizes acids and forms salts, thus—



These salts, ammonium chloride and ammonium sulphate, have definite properties, and are strictly analogous to sodium salts. Thus, we have—

Sodium Salts	Ammonium Salts
NaCl	NH <sub>4</sub> Cl
NaNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>
Na <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
etc.	etc.

Hence, it is believed that ammonium compounds contain a group of atoms which acts like an atom of a metal. This group of atoms is called **ammonium**, and its formula is NH<sub>4</sub>. Ammonium has never been separated from its compounds, or if it has it is so unstable that it immediately decomposes into ammonia gas and hydrogen. So also ammonium hydroxide has never been obtained free, for it decomposes readily into ammonia gas and water, thus—



Ammonium is sometimes called a **radical**, because it is the root or foundation of a series of compounds. It is likewise called a hypothetical metal, because its existence is assumed and it acts chemically like metals.

**Ammonium Chloride** is prepared by passing ammonia gas into dilute hydrochloric acid, by mixing ammonium hydroxide and hydrochloric acid, or by letting the two gases mingle. The equation for the essential reaction is—

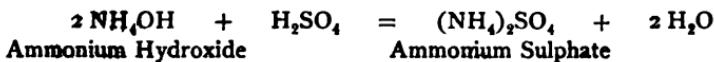


It is convenient to regard this compound as the ammonium salt of hydrochloric acid, as if it were formed by replacing the hydrogen of the acid by ammonium, just as sodium forms sodium chloride.

Ammonium chloride is a white, granular or crystalline solid, with a sharp, salty taste. It dissolves easily in water, and in so doing lowers the temperature markedly. When heated, it gradually breaks up into ammonia and hydrochloric acid, which reunite as the temperature falls. This kind of decomposition is called **dissociation**.

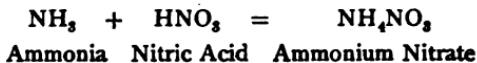
Large quantities of ammonium chloride are made at one stage of the manufacture of ammonium hydroxide by passing the gas into hydrochloric acid. The crude product is called "muriate of ammonia" to indicate its relation to muriatic (or hydrochloric) acid. It is largely used for charging Leclanché batteries, as an ingredient of soldering fluids, in galvanizing iron, and in textile industries. The crude salt is purified by heating it gently in a large iron or earthenware pot, with a dome-shaped cover; the ammonium chloride volatilizes easily and then crystallizes in the pure state as a fibrous mass on the inside of the cover, but the impurities remain behind in the vessel. The process of vaporizing a solid substance and then condensing the vapor directly into the solid state is called **sublimation**. It differs from distillation in that the substance does not pass through an intermediate liquid state. The product of sublimation is called a **sublimate**. Sublimed ammonium chloride is known as *sal ammoniac*.

**Ammonium Sulphate** is made by passing ammonia gas into sulphuric acid, or by adding ammonium hydroxide to the acid, thus—



The commercial salt is a grayish or yellowish solid. It is used as a constituent of fertilizers, since it is rich in nitrogen, and in making ammonium alum and other ammonium compounds.

**Ammonium Nitrate** is made by passing ammonia into nitric acid, or by allowing ammonia gas and the vapor of nitric acid to mingle, thus—



It is a white salt which forms beautiful crystals. It dissolves easily in water with a fall of temperature. Its chief use is in the preparation of nitrous oxide (see this compound).

**Ammonium Carbonate** is an impure salt as found in commerce, being a mixture of acid ammonium carbonate ( $\text{HNH}_4\text{CO}_3$ ) and a related compound. When pure and fresh it is transparent, but on exposure to the air it loses ammonia and turns white. It is used to prepare some kinds of baking powder, to scour wool, as a medicine, and to prepare smelling salts, since it gives off ammonia readily.

**Other ammonium compounds** are sodium ammonium phosphate or microcosmic salt ( $\text{HNaNH}_4\text{PO}_4$ ), ammonium sulphocyanate ( $\text{NH}_4\text{SCN}$ ), and ammonium sulphide ( $(\text{NH}_4)_2\text{S}$ ).

**Uses of Ammonia.**—Ammonia in the different forms is widely used as a cleansing agent, especially for the removal of grease, as a restorative in cases of fainting or of inhaling irritating gases, in dyeing and calico printing, and in the manufacture of dyestuffs, sodium carbonate, and ice. Its salts have many domestic, industrial, and agricultural uses.

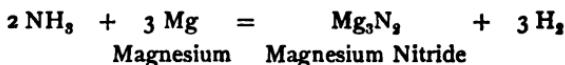
**The Use of Ammonia as a Refrigerant and in making Ice** depends upon the fact that many liquids in passing into a gas absorb heat. Liquefied ammonia (not the ordinary liquid, ammonia) changes rapidly into a gas when its temperature is raised or the pressure reduced. Hence, if anhydrous ammonia is allowed to flow through a pipe surrounded by brine, the ammonia evaporates in the pipe and cools the brine, which may be used as a refrigerant or for

making ice. In some cold storage houses, breweries, packing houses, and sugar refineries, this cold brine is pumped through pipes placed in the rooms where a low temperature is desired.

The construction and operation of an ice-making plant are essentially as follows : —

Liquefied ammonia is forced from a tank into a series of pipes which are submerged in an immense vat filled with brine. Large galvanized iron cans containing pure water to be frozen are immersed in the brine, which is being kept below the freezing point of water by the rapid evaporation of the ammonia in the pipes. In about sixty hours the water in the cans is changed into a cake of ice weighing about three hundred pounds. As fast as the ammonia gas forms in the pipes, it is removed by exhaust pumps into another tank, where it is reconddensed to liquefied ammonia and conducted, as needed, into the first tank to be used again. The ammonia is thus used over and over without appreciable loss. The pure water is sometimes obtained by condensing the exhaust steam from the boilers used to operate the machinery, though it usually comes from a deep well. Most ocean steamers have an ice plant, and in large cities in warm climates manufactured ice is a common commodity.

**Composition of Ammonia Gas.**—Numerous experiments show that ammonia gas has the composition expressed by the formula  $\text{NH}_3$ . (1) Dry ammonia gas passed over heated magnesium decomposes into hydrogen and nitrogen. The hydrogen may be collected and tested, but the nitrogen combines with the magnesium, forming a yellowish green powder called magnesium nitride, thus —



These facts show that ammonia contains nitrogen and hydrogen. (2) If a bottle is filled with chlorine gas and plunged mouth downward into a vessel containing ammonium hydroxide, dense white fumes fill the bottle, the greenish chlorine gas disappears, and the liquid rises in the bottle ; after the bottle has stood mouth downward in a dish containing dilute hydrochloric acid (to neutralize the excess of ammonia), the gas in the bottle will be found to be nitrogen. The chlorine with-

draws the hydrogen from the ammonia of the ammonium hydroxide leaving the nitrogen free, thus—



(3) The same experiment, if performed accurately, shows that one volume of nitrogen combines with three volumes of hydrogen to form ammonia gas. A tube containing a known volume of chlorine is provided with a funnel through which concentrated ammonium hydroxide is dropped into the chlorine, until the reaction ceases (Fig. 22). After the excess of ammonia is neutralized with sulphuric acid, the volume

of nitrogen left is one third of the original volume of chlorine gas. Now hydrogen and chlorine combine in equal volumes, hence the volume of hydrogen withdrawn from the added ammonia must be equal to the original volume of chlorine. But this volume is three times the volume of nitrogen, therefore there must be three times as much hydrogen as nitrogen in ammonia gas. (4) When electric sparks are passed through ammonia gas, it is decomposed into nitrogen and hydrogen. Now if oxygen is added, and an electric spark passed through the mixture, the oxygen and hydrogen combine. The volume of the remaining nitrogen is one fourth of the mixture of nitrogen and hydrogen, hence the hydrogen must have been three fourths; that is, the volume of hydrogen in the original volume of ammonia was three times that of the nitrogen. (5) The gravimetric composition of ammonia gas is found by oxidizing it, and weighing the water and nitrogen, which are the only products. The result shows that fourteen parts of nitrogen combine with three parts of hydrogen. (6) The vapor density has been found to be 8.5. These facts require  $\text{NH}_3$  as the simplest formula for ammonia and 17 as its molecular weight. Independent experiments verify this molecular weight.

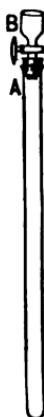


FIG. 22.—Apparatus for determining the composition of ammonia gas.

The only products. The result shows that fourteen parts of nitrogen combine with three parts of hydrogen. (6) The vapor density has been found to be 8.5. These facts require  $\text{NH}_3$  as the simplest formula for ammonia and 17 as its molecular weight. Independent experiments verify this molecular weight.

#### NITRIC ACID.

**Nitric Acid** is one of the most useful compounds of nitrogen. It was known to the alchemists, who used it

to prepare a mixture which dissolves gold. Nitric acid is used in the preparation of many nitrogen compounds.

**Formation of Nitric Acid.**—When moist animal or vegetable matter containing nitrogen decays *in the presence* of an alkali, nitric acid is formed; it is neutralized at once by the alkali, so nitrates—salts of nitric acid—are the final products. This chemical change is known as **nitrification**, and it is caused, or largely influenced, by minute living organisms called bacteria. Nitrification is constantly going on in the soil and is an exceedingly helpful process, since it transforms harmful waste matter into valuable plant food.

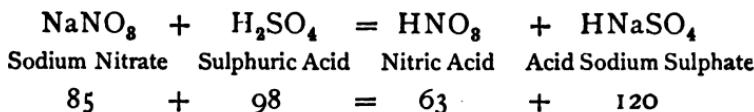
As a result of nitrification, there are vast deposits of nitrates, especially in desert regions and tropical countries. For example, potassium nitrate ( $\text{KNO}_3$ ) is found in the soils near large cities in India, Persia, and Egypt.

Nitric acid is formed in small quantities when electric sparks are passed through moist air. Hence nitric acid or its salts can be detected in the atmosphere after a thunder-storm.

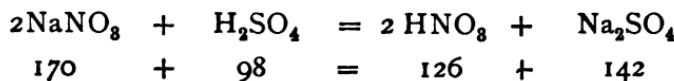
This chemical change is now being applied on a commercial scale in Norway. Electric sparks are passed through confined air and the products are forced into a tower. Here they are absorbed in water or in a solution of lime, thereby forming nitric acid or calcium nitrate. The latter may be made into sodium nitrate or used as a fertilizer.

**Preparation.**—Nitric acid is prepared in the laboratory by heating concentrated sulphuric acid with a nitrate, usually sodium or potassium nitrate. About equal weights of nitrate and acid are put into a glass retort and gently heated. The nitric acid distils into a receiver, which is kept cool by running water, ice, or moist paper. The

chemical change at a low temperature is represented by the equation —



But if the temperature is high and an excess of the nitrate is present, the equation is —



A high temperature, however, decomposes part of the nitric acid, hence excessive heat is usually avoided.

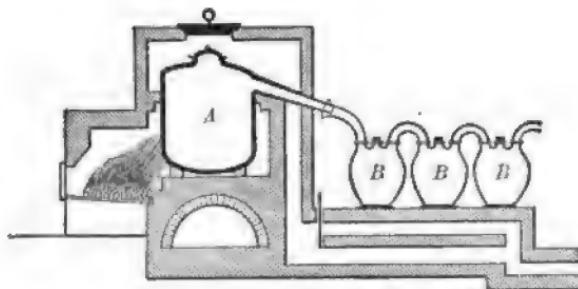


FIG. 23.—Apparatus for the manufacture of nitric acid.

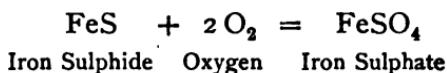
Nitric acid is manufactured on a large scale by heating sodium nitrate and sulphuric acid in a large cast-iron retort (*A*) connected with huge glass or earthenware bottles (*B*, *B*, *B*), arranged as shown in Figure 23; the last bottle is connected with a tower filled with coke over which water trickles to absorb the vapors which escape from the bottles. The acid vapors are also often absorbed in earthenware or glass tubes.

**Properties.** — Pure nitric acid is a colorless liquid, but the commercial acid is yellow or reddish, due to absorbed nitrogen compounds, chlorine, or iron compounds. It decomposes slowly in the sunlight or when heated, and a

brownish gas may often be seen in bottles of nitric acid. It absorbs water, and forms irritating fumes when exposed to the air. The specific gravity of the commercial acid is about 1.42, and it contains from 60 to 70 per cent of the real acid ( $\text{HNO}_3$ ), the rest being water.

If the water is removed by slowly distilling the commercial acid with concentrated sulphuric acid, the product contains from 94 to 99 per cent of the real acid and its specific gravity is about 1.51. When nitric acid is boiled, it loses either acid or water until the liquid contains approximately 68 per cent of nitric acid, and then it continues to boil unchanged at  $120^\circ\text{C}$ .

Nitric acid is very corrosive. It turns the skin a permanent yellow color, and may cause serious burns. Many organic substances are turned yellow and sometimes completely decomposed by it. It parts readily with its oxygen, especially when hot, and is therefore an energetic oxidizing agent. Charcoal burns brilliantly in hot acid, while straw, sawdust, hair, and similar substances are charred and even inflamed by it. Iron sulphide heated with nitric acid becomes iron sulphate, by the addition of oxygen, thus—



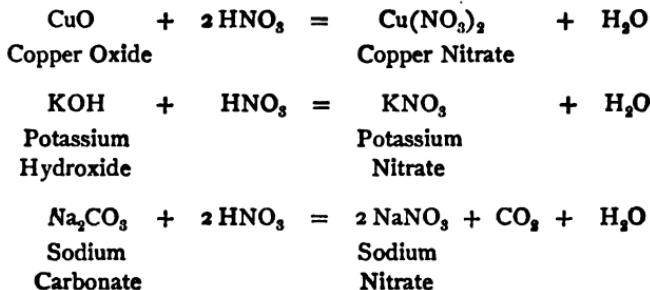
**Uses of Nitric Acid.**—Nitric acid is one of the common laboratory acids. Large quantities are used in the manufacture of nitrates, dyestuffs, sulphuric acid, nitro-glycerine, gun cotton, in the refining of gold and silver, and in etching copper plates.

**Composition of Nitric Acid.**—Although the alchemists knew and valued nitric acid, its composition was a mystery until Lavoisier showed in 1776 that it contained oxygen and probably nitrogen. Its exact composition was determined by Cavendish in 1784-1785, by passing electric sparks through a mixture of oxygen and nitrogen in the pres-

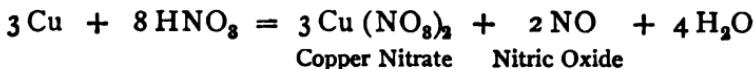
ence of water or caustic potash. The same facts had been observed, but not explained, by Priestley. Many independent experiments show that the composition of nitric acid is expressed by the formula  $\text{HNO}_3$ . (1) When electric sparks are passed through a bottle containing moist air or a solution of potassium hydroxide, the water becomes acid to litmus or the liquid will be found to contain a trace of potassium nitrate. (2) Nitric acid may be reduced to ammonia by nascent hydrogen, thus showing that the acid contains nitrogen. (3) Conversely, if a mixture of ammonia and air is passed over a mass of hot, porous platinum, nitric acid is formed. (4) If the acid is allowed to flow through a hot porcelain or clay tube, oxygen is one of the gaseous products.

**Nitrates.** — Nitric acid is monobasic and forms a series of well-defined salts called **nitrates**. The interaction of nitric acid and most metals is exceedingly vigorous, and for this reason, probably, the alchemists called the acid *aqua fortis* — strong water. The reaction varies with the metal, strength of the acid, temperature, and the presence of resulting compounds.

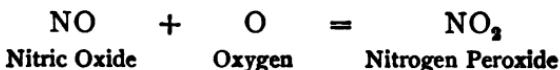
The solid product of the reaction is usually a nitrate, though some metals, such as tin and antimony, form oxides. The gaseous products are usually oxides of nitrogen, especially nitric oxide ( $\text{NO}$ ), which, however, quickly forms nitrogen peroxide ( $\text{NO}_2$ ) in the air. Hydrogen is never liberated so that it can be collected; probably it immediately reduces the nitric acid to another compound of nitrogen. Nitrates are also formed by the action of nitric acid upon oxides, hydroxides, and carbonates, thus —



When nitric acid is poured upon copper, the liquid bubbles violently and becomes hot, dense fumes of a reddish brown gas are given off, and the liquid turns blue owing to the dissolved copper nitrate. Other metals, such as zinc, iron, and silver, act in a similar way, though the nitrate is blue only in the case of copper. The usual equation for the chemical change with copper is —



When nitric oxide is exposed to the air, it changes at once into the reddish brown peroxide, thus —



Nitrates as a rule are very soluble in water. They behave in various ways when heated. Some, like sodium and potassium nitrates, lose oxygen and pass into nitrites; others, like copper nitrate, form an oxide of the metal, an oxide of nitrogen, and oxygen; and one, ammonium nitrate, decomposes into water and nitrous oxide ( $\text{N}_2\text{O}$ ). Since many nitrates, when heated, give up oxygen, they are powerful oxidizing agents. Potassium nitrate dropped on hot charcoal burns the charcoal vigorously and rapidly. This kind of chemical action is called **deflagration**.

**The Test for Nitrates** (and of course for nitric acid) is as follows: Add to the nitrate solution an equal bulk of concentrated sulphuric acid, and upon the cool mixture pour carefully a cold, dilute solution of fresh ferrous sulphate. A brown layer is formed where the two liquids meet.

**Nitrous Acid** ( $\text{HNO}_2$ ) has never been obtained in the free state, but its salts—the nitrites—are well known. Potassium nitrite ( $\text{KNO}_2$ ) and sodium nitrite ( $\text{NaNO}_2$ ) are formed by removing the oxygen from the corresponding nitrate by heating gently or by heating with lead. Nitrites give off brown fumes when treated with sulphuric acid, thus

being readily distinguished from nitrates. Nitrites are formed by the decomposition of organic matter, and the presence of a relatively large amount in drinking water indicates contamination by sewage.

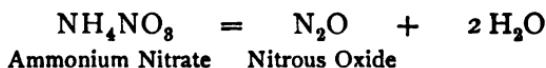
**Aqua Regia** is an old term which is still applied to a mixture of concentrated nitric and hydrochloric acids. The expression means "royal water," and indicates that the mixture dissolves gold and platinum—the noble metals. Its solvent power depends mainly upon the free chlorine which is produced in the mixture by the oxidizing action of the nitric acid. The product of the action of *aqua regia* on metals is always the chloride of the metal.

**Oxides of Nitrogen.**—There are five oxides of nitrogen:—

NAME.	FORMULA.	CHARACTERISTIC.
Nitrous oxide . . . . .	$\text{N}_2\text{O}$	Colorless gas
Nitric oxide . . . . .	NO	Colorless gas
Nitrogen trioxide . . . . .	$\text{N}_2\text{O}_3$	Blue liquid
Nitrogen peroxide . . . . .	$\text{NO}_2$	Brown gas
Nitrogen pentoxide . . . . .	$\text{N}_2\text{O}_5$	White solid

Only three of these are important, viz., nitrous and nitric oxides, and nitrogen peroxide.

**Nitrous Oxide** is one of the numerous decomposition products of nitric acid, but it is usually prepared by decomposing ammonium nitrate. This salt, if gently heated in a test tube provided with a delivery tube, first melts and then decomposes into water and nitrous oxide; the gas may be collected over warm water. The equation of the chemical change is—



This colorless gas has a sweet taste and a faint but pleasant odor. It is less soluble in hot than in cold water. The gas does not burn, but it supports the combustion of many burning substances, though not so vigorously as oxygen does. Sulphur, for example, will not burn in nitrous oxide, unless the sulphur is hot and well ignited at first. The most striking property of nitrous oxide is its effect on the human system. If breathed for a short time, it causes more or less nervous excitement, often manifested by laughter, and on this account the gas was called "laughing gas" by Davy. If breathed in large quantities, it slowly produces unconsciousness and insensibility to pain. The gas is often used when insensibility is desired for a short time, as in dentistry.

It is easily liquefied by cold and pressure, and is often used in this form to furnish the gas itself and to produce very low temperatures. It is a commercial article and is sold in small iron cylinders.

Nitrous oxide was discovered by Priestley in 1776; but its composition was not explained until 1799, when Davy, by an extensive study of its properties, proved it to be an oxide of nitrogen. In his enthusiasm Davy wrote a friend: "This gas raised my pulse upward of twenty strokes, made me dance about the laboratory as a madman, and has kept my spirits in a glow ever since." It is needless to say that the usual results are more quieting.

**The Composition of Nitrous Oxide** is shown as follows: By exploding equal volumes of nitrous oxide and hydrogen, only nitrogen remains, and its volume equals the original volume of nitrous oxide. The oxygen unites with the hydrogen to form water, and there is just enough oxygen to unite with a volume of hydrogen equal to the volume of the nitrous oxide. Therefore, the oxygen in the nitrous oxide must have been equal to half the volume of the nitrogen, since oxygen and hydrogen combine in the ratio of one to two. Furthermore, experiment has shown that the weights of equal volumes of nitrous oxide and nitrogen are in the ratio of 44 to 28. Therefore, the smallest part of oxygen united with the nitrogen must weigh 16; and since the nitrogen weighs 28, the formula must be  $\text{N}_2\text{O}$ .

**Nitric Oxide** has long been known, since it is the usual gaseous product of the interaction of nitric acid and metals. It is usually prepared by the interaction of copper and dilute nitric acid (sp. gr. 1.2). The equation for the complex chemical change is usually written thus—



The gas thus prepared is impure, and it is customary to use ferrous sulphate and nitric acid as a source of the pure gas.

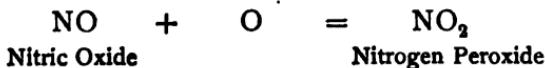
Nitric oxide is a colorless gas, but upon exposure to the air, it combines at once with oxygen, forming dense reddish brown fumes of nitrogen peroxide. The simplest equation for this change is—



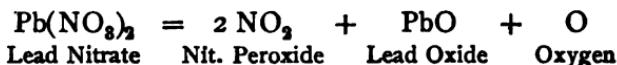
This property distinguishes nitric oxide from all other gases. It does not burn, nor does it support combustion unless the burning substance (*e.g.* phosphorus or sodium) introduced is hot enough to decompose the gas into nitrogen and oxygen, and then, of course, the liberated oxygen assists the combustion.

**The Composition of Nitric Oxide** is determined by heating iron or another metal in it. The oxygen of the oxide combines with the iron, and the nitrogen is left free. The resulting volume of nitrogen is half the volume of the nitric oxide taken. Hence nitric oxide contains equal volumes of nitrogen and oxygen. By an independent experiment the molecular weight is found to be 30. Hence the formula must be NO.

**Nitrogen Peroxide** is the reddish brown gas formed by the direct combination of nitric oxide and oxygen. Thus—



It is also produced by heating certain nitrates. Thus—

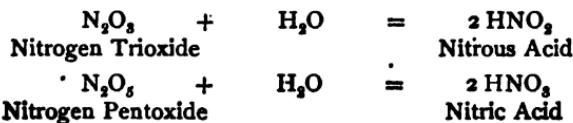


The fumes of nitrogen peroxide always appear when nitric acid and metals interact, but, as already stated, the fumes are not produced at first, being the result of a second chemical change when the real product, nitric oxide, comes in contact with oxygen of the air.

Nitrogen peroxide is poisonous. It dissolves in water; it also dissolves in concentrated nitric acid, forming **fuming nitric acid**.

At about  $-12^{\circ}\text{C}$ . nitrogen peroxide is a colorless solid. At about  $-10^{\circ}\text{C}$ . it is a yellowish liquid, and as the temperature rises the color grows darker, until at  $22^{\circ}\text{C}$ . the liquid boils and gives off the familiar reddish brown gas. Above  $140^{\circ}\text{C}$ . this gas begins to lose its color; at higher temperatures the brown color entirely disappears, and nitric oxide and oxygen are produced. Experiments show that the colorless gas at  $22^{\circ}\text{C}$ . has the formula  $\text{N}_2\text{O}_4$ , whence the name **nitrogen tetroxide**, often used. The brown gas at about  $140^{\circ}\text{C}$ . has the formula  $\text{NO}_2$ .

**Nitrogen Trioxide**,  $\text{N}_2\text{O}_3$ , and **Nitrogen Pentoxide**,  $\text{N}_2\text{O}_5$ , are unstable compounds and have no practical importance. They are the anhydrides of nitrous and nitric acids, thus—



### EXERCISES.

1. Name several sources of ammonia gas. How is ammonia gas prepared in the laboratory? Give the equation for the reaction. State its important properties.
2. What is ammonium hydroxide? How is it prepared on a large scale? Summarize its properties. What are its uses?
3. What is the meaning and significance of (a) volatile alkali,

(b) anhydrous ammonia, (c) spirits of hartshorn, (d) *sal volatile*,  
 (e) muriate of ammonia, (f) *sal ammoniac*, (g) *aqua fortis*?

4. Why is  $\text{NH}_3$  the formula of ammonia gas?
5. Give several tests for (a) ammonia, and (b) nitric acid.
6. What different meanings may the word *ammonia* have? What is ammoniacal liquor? Gas liquor? *Aqua ammonia*? Ammonium hydrate? Ammonia of commerce? Ammonia water?
7. How is ammonia gas liquefied? Describe the manufacture of ice by liquid ammonia.
8. Develop the topics: (a) ammonium is a radical; (b) nitric acid is an oxidizing agent; (c) nitrates are unstable; (d) fuming nitric acid.
9. Give the formula, method of preparation, properties, and uses of (a) ammonium chloride, (b) ammonium nitrate, (c) ammonium sulphate, (d) ammonium carbonate.
10. How is nitric acid formed (a) in the soil, (b) in the air? How is it prepared (a) in the laboratory, (b) on a large scale? Summarize (a) the physical properties of nitric acid, and (b) its chemical properties. For what is it used?
11. What is the formula of nitric acid? Summarize the evidence of its composition.
12. What are nitrates? How are they formed? What is the effect of heat upon (a) potassium nitrate, (b) copper nitrate, (c) ammonium nitrate? Give other properties of nitrates. What is the test for nitrates?
13. What are nitrites? How are they formed? How are they distinguished from nitrates?
14. What is *aqua regia*? For what is it used? Why so called? What is the chemical action of *aqua regia* on gold? Upon what property of nitric acid does its chemical action depend?
15. Give the names and formulas of the five oxides of nitrogen. Describe the preparation of nitrous oxide. State briefly its properties. For what is it used? Who discovered it? What did Davy call it? Why? Summarize the evidence of the composition of nitrous oxide.
16. Describe the preparation of nitric oxide. State the equation for the reaction. What are its properties?
17. How is nitrogen peroxide prepared? State its properties. How is it readily distinguished from all other oxides of nitrogen? What two formulas have been given to nitrogen peroxide? Why?
18. What is (a) nitric oxide, (b) nitrous oxide, (c) nitrogen per-

oxide, (d) nitrogen tetroxide, (c) nitrogen trioxide, (d) nitrogen monoxide, (e) nitrogen pentoxide?

19. State the equation for the preparation of (a) nitric acid at a low temperature, (b) nitric acid at a high temperature, (c) ammonium chloride, (d) ammonium hydroxide from water and ammonia, (d) nitrous oxide, (e) nitrogen peroxide, (f) copper nitrate.

20. Define and illustrate (a) sublimation, (b) sublimate, (c) nitrification, (d) deflagration, (e) nitrate, (f) ammonium compound.

21. What is the valence of nitrogen in ammonia gas? In ammonium? In ammonium hydroxide?

22. (a) Why are there no acid nitrates? (b) What is the valence of nitrogen in nitric acid, copper nitrate, nitrous oxide, nitric oxide, nitrogen peroxide, nitrogen trioxide, nitrogen pentoxide?

### PROBLEMS.

1. How many grams of ammonia gas can be obtained from 2140 gm. of ammonium chloride by heating with lime?

2. Calculate the percentage composition of (a) ammonium chloride, (b) ammonium hydroxide, (c) ammonium sulphate, (d) ammonium nitrate.

3. Calculate the simplest formula of the compounds having the percentage composition (a) N = 82.35, H = 17.64; and (b) N = 26.17, Cl = 66.35, H = 7.48.

4. Calculate the percentage composition of (a) nitric acid, (b) potassium nitrate ( $KNO_3$ ), (c) sodium nitrate.

5. How many grams of nitric acid can be obtained by heating a kilogram of sodium nitrate with sulphuric acid at a low temperature?

6. If the specific gravity of a sample of nitric acid is 1.522, (a) what will 100 cc. weigh, and (b) what volume must be taken to weigh 100 grams?

7. Calculate the simplest formula of the substances having the composition (a) O = 76.19, H = 1.58, N = 22.22; (b) N = 13.86, K = 38.61, O = 47.52.

## CHAPTER XIII.

### PROPERTIES OF GASES—GAY-LUSSAC'S LAW OF GAS VOLUMES—AVOGADRO'S HYPOTHESIS—VAPOR DENSITY AND MOLECULAR WEIGHT—MOLECULAR WEIGHTS AND ATOMIC WEIGHTS—MOLECULAR FORMULA—MOLECULAR EQUATIONS—VALENCE.

**Properties of Gases.**—Extensive study of gases shows that they all conform to simple laws. Thus we have already seen that they behave uniformly with changes of pressure (Boyle's law) and with changes of temperature (Charles's law). Other simple relations prevail.

**Gay-Lussac's Law.**—Gases combine by volume in simple ratios. Experiment has revealed the following facts about the—

#### COMBINATION OF GASES BY VOLUME.

VOLUMES OF COMPONENTS.	VOLUMES OF PRODUCTS.
2 vol. hydrogen 1 vol. oxygen	2 vol. water vapor
1 vol. chlorine 1 vol. hydrogen	2 vol. hydrochloric acid gas
3 vol. hydrogen 1 vol. nitrogen	2 vol. ammonia gas
2 vol. nitrogen 1 vol. oxygen	2 vol. nitrous oxide gas
2 vol. nitrogen 3 vol. oxygen	2 vol. nitrogen trioxide gas

Additional illustrations will be given in later chapters. The simple ratio which exists between the gas volumes, whether components or products, has been found to be true of all gases. The law was pointed out in 1808 by Gay-Lussac, who stated the relation substantially as follows:—

*Gases combine in volumes which bear a simple ratio to each other and to that of the product.*

By "a simple ratio" we mean one made up of small whole numbers. As a rule, the product occupies two unit volumes.

**Avogadro's Hypothesis.** — In 1811 an Italian physicist proposed an hypothesis to account for the similar behavior of gases. At that time the properties of gases were not generally known, and the views of Avogadro were overlooked until about 1860. Since then the hypothesis has been helpful in explaining many facts, and it is generally accepted by chemists as a very probable assumption. It may be stated thus:—

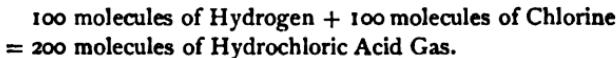
*There is an equal number of molecules in equal volumes of all gases at the same temperature and pressure.*

This statement means that there is the same relation between molecules as between equal volumes of gases. A liter of hydrogen weighs 0.0898 gm. and a liter of oxygen at the same temperature and pressure weighs 1.43 gm.; i.e. a liter of oxygen weighs sixteen times as much as a liter of hydrogen. Now according to Avogadro's hypothesis a liter of hydrogen and a liter of oxygen at the same temperature and pressure contain the same number of molecules, though we do not know how many. Suppose, however, that each liter contained one thousand molecules. Therefore, since

a thousand molecules of oxygen weighs 16 times more than a thousand molecules of hydrogen, a single molecule of oxygen must weigh 16 times more than a single molecule of hydrogen. Therefore, in general, in order to find how much heavier any gaseous molecule is than a hydrogen molecule, it is only necessary to compare the weights of equal volumes of hydrogen and the gas under examination.

An application of Avogadro's hypothesis is made in course of the following argument, which proves that a molecule of hydrogen consists of two atoms : —

One volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid gas. Suppose the volume of hydrogen contained 100 molecules. Then, according to Avogadro's hypothesis, the equal volume of chlorine will contain 100 molecules, while the two volumes of the product will contain 200 molecules of hydrochloric acid gas. That is —



Now every molecule of hydrochloric acid gas contains at least one atom each of hydrogen and chlorine, and the 200 molecules must contain 200 atoms each of chlorine and hydrogen. Therefore each molecule of hydrogen and of chlorine must contain at least two atoms, since the 100 hydrogen and the 100 chlorine molecules provide the 200 hydrogen atoms and the 200 chlorine atoms in the 200 molecules of hydrochloric acid gas. There is no evidence that the hydrogen or the chlorine molecule contains more than two atoms.

**Vapor Density and Molecular Weight.** — It was stated in a previous chapter that a molecular weight is the sum of the weights of the atoms in the molecule. But this method of finding the molecular weight is useless, unless we first know the formula, and in many cases the formula cannot be chosen until after the molecular weight has been found by several methods. Hence, the determination of molecular weights is an important matter. In the case

of gaseous or volatile elements and compounds, it is often accomplished by finding the vapor density of the substance. There is a direct and simple relation between molecular weight and vapor density. By **vapor density** we mean the ratio of the weight of a gas to the weight of an equal volume of hydrogen at the same temperature and pressure. Thus, the vapor density of steam is 9, because experiment shows that it weighs 9 times more than an equal volume of hydrogen under the same conditions of temperature and pressure. Therefore the molecular weight of steam is 9 times the molecular weight of hydrogen. But the molecular weight of hydrogen is 2, since its molecule contains two atoms each weighing 1. Therefore, the molecular weight of steam is 18, or twice the vapor density. The general fact that **the molecular weight of a compound in the gaseous state is twice its vapor density** is illustrated by the following table showing the —

#### RELATION BETWEEN VAPOR DENSITY AND MOLECULAR WEIGHT.

GAS.	VAPOR DENSITY.	MOLECULAR WEIGHT.
Carbon dioxide . . . .	22	44
Ammonia . . . . .	8.5	17
Hydrochloric acid . . .	18.25	36.5
Water vapor (steam) . .	9	18

**Other Methods of determining Molecular Weights.**— Some substances cannot be vaporized without decomposition. The molecular weights of such substances cannot, of course, be found by the vapor density method. If a substance dissolves without decomposition, its molecular weight can be determined by the boiling-point or freezing-point method. No experimental method is known for determining the molecular weight of a substance in the solid state. The molecular weight of a substance in the solid state is assumed to have the same value as that found by the usual methods.

**Determination of Atomic Weights.** — The atomic weight of an element, as already stated, is a relative weight. It is a number expressing the relation of the weight of an atom of a given element to the weight of an atom of some element chosen as a standard. Thus, if we say that the atomic weight of nitrogen is 14, we mean that the relation between the weight of the nitrogen atom and that of the hydrogen atom is 14 to 1, if we adopt the hydrogen atom as the standard atom; or we mean that the relation between the weight of the nitrogen atom and that of the oxygen atom is 14 to 16, if we adopt the oxygen atom as the standard. The approximate atomic weights are usually expressed in round numbers, and do not vary much with the standard. Wherever exact atomic weights are used in this book, the oxygen standard is the basis. (See International and Approximate Atomic Weights, Appendix, § 5.)

In Chapter IX it was stated that the determination and selection of atomic weights are based on several principles. This subject can now be appropriately considered.

Analysis of compounds gives their composition in per cent. If the per cents are restated in a certain way, equivalents are obtained. But equivalents are not used to express composition, because they do not harmonize with facts and theories. For example, (a) the sum of the equivalents of the elements in a compound does not always equal the molecular weight, and (b) certain elements have two equivalents. Now the numbers selected as atomic weights do harmonize with the system of facts and theories adopted in chemistry for expressing the quantitative relations of the elements. The atomic weight of an element is equal to or a multiple of its equivalent; it is also the smallest weight of an element

which is contained in a molecule of many representative compounds.

One method of selecting the atomic weight is illustrated by the case of chlorine, which has the atomic weight 35.5. The molecular weights of several chlorine compounds are found by the vapor density method. The compounds are analyzed to find the number of grams of chlorine in that number of grams of the compound equal to the determined molecular weight. And the highest common factor of these weights of chlorine is taken as the atomic weight of the element. A concise view of the method is shown in the following —

TABLE OF CHLORINE COMPOUNDS.

COMPOUND.	MOLECULAR WEIGHT.	WEIGHT OF CHLORINE.	H. C. F.
Hydrochloric acid . . . . .	36.5	35.5	1 × 35.5
Chlorine peroxide . . . . .	67.5	35.5	1 × 35.5
Cyanogen chloride . . . . .	61.5	35.5	1 × 35.5
Chlorine gas . . . . .	71	71	2 × 35.5
Chlorine monoxide . . . . .	87	71	2 × 35.5
Phosphorus trichloride . . .	137.5	106.5	3 × 35.5
Chloroform . . . . .	119.5	106.5	3 × 35.5
Carbon tetrachloride . . . .	170	142	4 × 35.5

None of these compounds contains a smaller weight of chlorine than 35.5; *i.e.* 35.5 is the atomic weight of chlorine.

Atomic weights can be determined accurately by analysis if we know the number of atoms which combine to form a molecule of the compound analyzed. Thus, the Belgian chemist, Stas, who made masterly determinations of atomic weights, found that 121.4993 gm. of silver

chloride were formed by burning 91.462 gm. of silver in chlorine. He knew that one atom of silver and one of chlorine unite to form silver chloride; he also accepted 35.453 as the atomic weight of chlorine. Hence, he calculated the atomic weight of silver thus —

$$121.4993 - 91.462 = 30.0373,$$

which is the weight of the chlorine used.

Therefore —

$$91.462 : 30.0373 :: x : 35.453, \quad x = 107.95,$$

which was accepted as the atomic weight of silver.

Approximate atomic weights of the solid elements, especially the metals, may be found by applying the **law of specific heats**. This law was announced by Dulong and Petit in 1819. It is stated as follows: —

*The product of the specific heat and atomic weight of the solid elements is approximately 6.25.*

By **specific heat** we mean the quantity of heat necessary to raise the temperature of a substance one degree compared with the quantity necessary to raise the temperature of the same weight of water one degree. If the same quantity of heat is imparted to equal weights of water and mercury, the temperature of the mercury will be much higher — about 32 times higher than that of the water. That is, the mercury requires only about  $\frac{1}{32}$  as much heat as the water. In other words, the specific heat of mercury is  $\frac{1}{32}$ , or 0.0312. The specific heat of other elements is readily found.

The constant quantity found by multiplying the specific heat by atomic weight is approximately 6.25. This relation is illustrated by the following —

TABLE OF SPECIFIC HEATS.

ELEMENT.	SPECIFIC HEAT.	ATOMIC WEIGHT.	PRODUCT.
Calcium . . . . .	0.170	40	6.8
Copper . . . . .	0.095	63.5	6.04
Iron . . . . .	0.114	56	6.38
Lead . . . . .	0.031	207	6.41
Potassium . . . . .	0.166	39	6.47
Sodium . . . . .	0.293	23	6.73
Sulphur . . . . .	0.178	32	5.7
Tin . . . . .	0.055	119	6.54
Zinc . . . . .	0.094	65.4	6.15

The use of this law in checking atomic weights may be illustrated as follows: The specific heat of silver is found by experiment to be 0.057; if 6.25 is divided by this number, the quotient is approximately 109. This result agrees approximately with 107.88—the accepted atomic weight of silver. Again, the specific heat of mercury is 0.0312; if 6.25 is divided by this number, the quotient, 200, indicates that the atomic weight of mercury is 200—a value obtained by other methods. This law has been of assistance in the final selection of the approximate atomic weight of several elements. Thus, the atomic weight of uranium was finally accepted as about 238 instead of 119. Both values agreed with analyses, but only the former conformed to Dulong and Petit's law.

The plan followed in determining the atomic weight of zinc illustrates the methods actually used.

(a) When zinc interacts with dilute hydrochloric or sulphuric acid, hydrogen is liberated; and if a known weight of zinc is used, the weight of zinc needed to liberate 1 gm. of hydrogen is easily calculated. This number, as we have already seen, is the equivalent of zinc (see Equivalents, Chapter IX). Now if one atom of zinc replaces one atom

of hydrogen, then the atomic weight of zinc and the atomic weight of hydrogen will have the same ratio as the weight of zinc and the weight of hydrogen found by experiment. According to experiment the equivalent of zinc is about 32.5. This is its relation, atom for atom, to hydrogen, and, thus far, is its atomic weight.

(b) When zinc and hydrochloric acid interact, zinc chloride is formed. If it is analyzed, the proportion of zinc to chlorine is about 32.5 to 35.5. If the elements combine, atom for atom, the atomic weight of zinc is 32.5 (assuming that 35.5 is the atomic weight of chlorine).

(c) When zinc is burned in air, zinc oxide is formed. If this compound is analyzed, the proportion of zinc to oxygen is about 65 to 16. If the elements combine atom for atom, the atomic weight of zinc is about 65 (assuming that 16 is the atomic weight of oxygen).

(d) According to these three determinations, the atomic weight of zinc is 32.5 or 65. We have assumed that the elements unite atom for atom in each compound. This is an incorrect assumption, because an atom of zinc cannot have two different weights — 32.5 and 65. If the atomic weight is 32.5, zinc oxide must consist of one atom of oxygen and two of zinc. But if the atomic weight is 65, zinc chloride must consist of two atoms of chlorine and one of zinc, and two atoms of hydrogen must have been replaced by one of zinc.

(e) The molecular weight of zinc chloride is found by the vapor density method to be about 133. If zinc chloride consists of two atoms of chlorine and one of zinc (weighing 65), its molecular weight is about 136. In other words, it is evident that our assumption regarding the number of atoms in zinc chloride is highly probable.

(f) We are not absolutely positive, however, that the zinc in a molecule of zinc chloride may not be one atom weighing 65, or two atoms weighing 32.5 each. But the atomic weight of zinc determined by applying the law of specific heats is 66.4 (*i.e.*  $6.25 + 0.094$ ). This shows clearly that the atomic weight of zinc is approximately 65.

**Molecular Formula.** — The simplest formula of a compound is found by dividing the percentage of each element by its atomic weight (and reducing the quotients to the smallest whole numbers, if necessary). But the simplest formula may not be the molecular formula; that is, it may not express the composition *and number of atoms* in a mole-

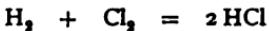
cule of the compound in the gaseous state. Every formula, however, is designed to be a molecular formula. Since the molecular weight of a compound is twice its vapor density, the molecular formula can be calculated from the simplest formula. Thus, the simplest formula of a compound of carbon and hydrogen was found to be  $\text{CH}_2$ . Its vapor density was found to be 81.4. Hence its molecular weight must be 162.8, which is nearly twelve times that corresponding to  $\text{CH}_2$ . Therefore the molecular formula is  $\text{C}_{12}\text{H}_{24}$ . Molecular formulas of other compounds may be similarly found.

**Molecular Equations.** — Equations which represent reactions between gases are sometimes written as **molecular equations**. Such equations represent changes as taking place between the smallest possible physical units, that is, between molecules. The molecular equation for the formation of water from hydrogen and oxygen is —

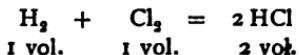


It is read thus : Two molecules of hydrogen unite with one molecule of oxygen to form two molecules of water. Since most elementary gases consist of molecules, such an equation is strictly correct. It should be noted, however, that the proportions are the same as in the simpler form of the equation. For practical purposes the molecular equation is preferable only in the case of gases.

Molecular equations are sometimes called **volume or gas equations**, because such equations tell at a glance the volumes involved in the reaction. Thus —



means that one volume each of hydrogen and chlorine unite to form two volumes of hydrochloric acid gas. This equation is sometimes written —



**Valence.** — An examination of many formulas obtained by the principles just discussed shows certain regularities. Take, for example, some binary compounds of hydrogen. They fall into four groups, thus—

I.	II.	III.	IV.
HCl	H <sub>2</sub> O	H <sub>3</sub> N	H <sub>4</sub> C
HBr	H <sub>2</sub> S	H <sub>3</sub> P	H <sub>4</sub> Si

Obviously, the atoms of these elements differ in their power of combining with hydrogen atoms. Some unite with one atom, some with two atoms, and so on. Atoms of other elements besides those in the above list differ in their combining power. The power of atoms of an element to hold in combination a certain number of other atoms is called the **valence** or **quantivalence** of the element. The valence of hydrogen is always one. Elements which combine atom for atom with one atom of hydrogen have the valence one, and are called **univalent elements** or **monads**; sodium and potassium are always univalent, and so is chlorine in hydrochloric acid. Elements which combine with two atoms of hydrogen have the valence two, and are called **bivalent elements** or **dyads**; oxygen, magnesium, and sulphur are bivalent elements. So, also, some elements like aluminium, are **trivalent** or **triads**; others, like carbon and silicon, are **quadrivalent** or **tetrads**; and some, like the nitrogen in nitric acid, are **quinquivalent** or **pentads**. Elements of the same valence combine with or replace each other atom for atom. Thus, one atom of sodium replaces one atom of hydrogen in hydrochloric acid; and one atom of oxygen combines with one atom of magnesium. Elements of different valence form compounds in which usually the total valence of the atoms of each element is equal. Thus,

a dyad combines with two monads (as in  $H_2O$ ), a triad with three monads (as in  $NH_3$ ), two triads with three dyads (as in  $Al_2O_3$ ), one tetrad with two dyads (as in  $CS_2$ ), and so on.

Radicals have a valence, since in chemical changes they act like atoms. The valence of ammonium ( $NH_4$ ) is one, and of hydroxyl ( $OH$ ) is one. Thus,  $NH_4Cl$  is the formula of ammonium chloride,  $NaOH$  of sodium hydroxide, but  $Ca(OH)_2$  of calcium hydroxide.

The valence of certain elements and radicals is as follows:

TABLE A.—VALENCE OF CERTAIN ELEMENTS.

NAME.	SYMBOL.	VALENCE.	NAME.	SYMBOL.	VALENCE.
Aluminium . . .	Al	III	Lead . . .	Pb	II
[Ammonium] . . .	[NH <sub>4</sub> ]	I	Magnesium . .	Mg	II
Barium . . .	Ba	II	Mercury (ous) .	Hg	I
Bismuth . . .	Bi	III	Mercury (ic) .	Hg	II
Calcium . . .	Ca	II	Potassium . .	K	I
Chromium . . .	Cr	III	Silver . . .	Ag	I
Copper (ous) . .	Cu	I	Sodium . . .	Na	I
Copper (ic) . .	Cu	II	Tin (ous) . .	Sn	II
Iron (ous) . . .	Fe	II	Tin (ic) . . .	Sn	IV
Iron (ic) . . .	Fe	III	Zinc . . .	Zn	II

TABLE B.—VALENCE OF CERTAIN ELEMENTS AND RADICALS.

NAME	SYMBOL OR FORMULA.	VALENCE.	NAME.	SYMBOL OR FORMULA.	VALENCE.
Bromide . . .	Br	I	Nitrate . . .	NO <sub>3</sub>	I
Carbonate . . .	CO <sub>3</sub>	II	Nitrite . . .	NO <sub>2</sub>	I
Chlorate . . .	ClO <sub>3</sub>	I	Oxide . . .	O	II
Chloride . . .	Cl	I	Permanganate	MnO <sub>4</sub>	I
Chromate . . .	CrO <sub>4</sub>	II	Phosphate . .	PO <sub>4</sub>	III
Dichromate . .	Cr <sub>2</sub> O <sub>7</sub>	II	Silicate . . .	SiO <sub>3</sub>	II
Fluoride . . .	F	I	Sulphate . . .	SO <sub>4</sub>	II
Hydroxide . . .	OH	I	Sulphide . . .	S	II
Iodide . . .	I	I	Sulphite . . .	SO <sub>3</sub>	II
Manganate . .	MnO <sub>4</sub>	II	Sulphite (acid)	HSO <sub>3</sub>	I

Formulas may be written by using these tables. Suppose the formula of magnesium chloride is desired. From table A the valence of magnesium is found to be II, and from table B the valence of chlorine in chlorides is found to be I. Remembering the rule that in most compounds the total valence of the atoms of each element is equal, it is necessary to have two atoms of chlorine and one of magnesium; hence the formula is  $MgCl_2$ . Again, suppose we wish the formula of lead nitrate. From the tables the valence of lead is II and of the  $NO_3$ -group is I. Therefore it is necessary to have two  $NO_3$ -groups for one atom of lead, and the formula is  $Pb(NO_3)_2$ . Similarly, the formula of aluminium oxide is  $Al_2O_3$ , because 2 and 3 are the least number of atoms of Al and O which give equal valence (VI in each case). Formulas of acids may be written by prefixing the correct number of hydrogen atoms to the atom or group in table B. Thus,  $HNO_3$  is the formula of nitrous acid.

Some chemists prefer to regard valence as the quotient obtained by dividing the atomic weight by the equivalent weight. For example, the valence of oxygen is 2, the quotient of  $16 \div 8$ . Such a view is not inconsistent with the one generally held, because valence is the direct outcome of composition.

The valence of elements may be represented in several ways, e.g.

$H'$ ,  $H -$ ,  $-O-$ ,  $O =$ ,  $N -$ . Sometimes formulas are written to show the valence, e.g.—

$\nearrow H$   
Hydrochloric acid,  $H - Cl$ , Water,  $H - O - H$ , Ammonia,  $N - H$ .

$\searrow H$

Such formulas are called **structural or graphic formulas** to distinguish them from the ordinary or **empirical formulas**.

### EXERCISES.

1. Review (a) Boyle's law, and (b) Charles's law.
2. State and illustrate Gay-Lussac's law.
3. Give a brief account of (a) Gay-Lussac, (b) Avogadro, (c) Stas.

4. State and illustrate Avogadro's hypothesis.
5. What is the relation of the molecular weight of a gas to (a) the molecular and (b) the atomic weight of hydrogen?
6. (a) State the argument proving that a molecule of hydrogen consists of two atoms. (b) Apply the same argument to oxygen.
7. What is the relation between molecular weight and vapor density? Illustrate your answer. What application is made of this relation?
8. Why is the formula of water  $H_2O$  and not HO or  $H_2O_2$ ?
9. Why is the formula of ozone  $O_3$ ?
10. (a) How are molecular weights determined? (b) How are atomic weights found from molecular weights?
11. Illustrate the method of determining atomic weights by chemical analysis.
12. What is a molecular formula? What is the molecular formula of oxygen, nitrogen, chlorine, and hydrogen? How is a molecular formula determined? Illustrate your answer.
13. What is a molecular equation? Give two illustrations. How does it differ from an ordinary chemical equation? Of what use are such equations? ✓
14. Define (a) valence, (b) monad, dyad, triad, tetrad, pentad, (c) univalent element, bivalent element, (d) saturated compound, (e) unsaturated compound. ✓
15. What is the valence of hydrogen? Why? Of oxygen? Why? How may valence be found by inspecting a binary formula? What is the valence of  $NH_4$  and  $OH^-$ ?
16. Illustrate the ways valence may be represented.
17. Distinguish between structural and empirical formulas.
18. Write the formula of the chloride of potassium, sodium, silver, copper (ous), copper (ic), mercury (ous), mercury (ic), iron (ous), iron (ic), zinc, tin (ous), tin (ic), calcium, barium, magnesium, bismuth, aluminium, ammonium, lead. ✓
19. Write the formula of the sulphate of K, Na, Ag, Cu, Fe (ous), Zn, Pb, Ca, Ba, Mg, Cr, Al,  $NH_4$ . ✓
20. Write the formula of manganese dioxide, ammonium fluoride, sodium silicate, potassium manganate, barium phosphate, zinc iodide, ammonium chromate, silver chromate, magnesium oxide, sodium dichromate, aluminium chloride, ferrous bromide, calcium phosphate, mercurous nitrate. ✓

21. Write the formula of ferrous carbonate, aluminium phosphate, calcium fluoride, sodium permanganate, phosphoric acid, silicic acid, sulphurous acid, nitrous acid, chromic acid, hydriodic acid, carbonic acid.

### PROBLEMS.

1. The vapor densities of certain gases are as follows: (a) hydrochloric acid 18.25, (b) chlorine 35.5, (c) ammonia 8.5, (d) nitrogen 14, (e) steam 9. Calculate the molecular weight of each.

2. Calculate the simplest formula of the compounds which have the indicated composition: (a) N = 82.353, H = 17.647; (b) O = 30, Fe (iron) = 70; (c) H = 1, C = 12, K (potassium) = 39, O = 48.

3. A liter of sulphurous oxide gas ( $\text{SO}_2$ ) weighs 2.8672 gm. What is the molecular weight of this compound?

4. If 1500 cc. of carbon monoxide gas (CO) weigh 1.8816 gm., what is the molecular weight of the compound?

5. Calculate the molecular formula of the compounds corresponding to the following data: (a) C = 73.8, H = 8.7, N = 17.1, vapor density = 80.2; (b) C = 92.3, H = 7.7, vapor density = 38.8; (c) C = 39.9, H = 6.7, O = 53.4, vapor density = 30.5.

6. What volumes of factors and products are represented by the equations (a)  $\text{H}_2 + \text{Cl}_2 = 2 \text{ HCl}$ , (b)  $2 \text{ H}_2 + \text{O}_2 = 2 \text{ H}_2\text{O}$ , (c)  $3 \text{ H}_2 + \text{N}_2 = 2 \text{ NH}_3$ , (d)  $\text{N}_2 + \text{O}_2 = 2 \text{ NO}$ , (e)  $2 \text{ NO} + \text{O}_2 = 2 \text{ NO}_2$ ?

7. If 20 l. of hydrogen are allowed to interact with 10 l. of chlorine, (a) how many liters of hydrochloric acid gas are produced, and (b) which gas and how much remains?

8. How many liters of hydrogen gas can be obtained from 4 l. of hydrochloric acid gas?

9. If 91.462 gm. of silver, when heated in chlorine, yield 121.4993 gm. of silver chloride, what is the atomic weight of chlorine? (Assume Ag = 108.)

10. How many liters of the component gases can be obtained by the decomposition of 6 l. of ammonia gas?

11. Find the simplest formulas of the substances having the following composition: (a) H = 1.58, N = 22.22, O = 76.19; (b) O = 47.52, N = 13.86, K = 38.61.

12. A certain weight of copper oxide, when heated in a current of hydrogen, lost 59.789 gm. of oxygen and formed 67.282 gm. of water. (a) If O = 16, what is the atomic weight of hydrogen? (b) If H = 1, what is the atomic weight of oxygen?

## CHAPTER XIV.

### CARBON AND ITS OXIDES—CYANOGEND.

**Occurrence of Carbon.**—Uncombined carbon is found pure in nature as diamond and graphite; in a more or less impure state it occurs as coal and similar substances, which are included in the term *amorphous carbon*. Carbon forms a vast number of compounds, natural and artificial. Combined with hydrogen and oxygen, and occasionally with nitrogen also, it is an essential constituent of plants and animals. Meat, starch, fat, sugar, wood, cotton, paper, soap, wool, wax, flour, albumen, and bone contain carbon. It is also a component of carbon dioxide and of carbonates, such as limestone, chalk, and marble. Illuminating gases, kerosene and other products of petroleum, turpentine, alcohol, chloroform, ether, and similar liquids are compounds of carbon. It is estimated that 0.22 per cent of the weight of the earth's crust is carbon.

**Diamond** is pure crystallized carbon. It is found in only a few places in the earth. When taken from the mine, diamonds are rough-looking stones; some are crystals, some are rounded like peas, and many are irregular; they must be cut and polished to bring out the luster and make them sparkle (Fig. 24). The highly prized diamonds are colorless and without a flaw, and are said to be "of the first water"; yellow ones from South Africa are common, and occasionally a blue, pink, red, or green one is found; a very impure variety is black.

The diamond is insoluble in all liquids at the ordinary temperature, has the high specific gravity of 3.5, and is the hardest known substance.

It is brittle and may be shattered by a blow with a hammer.

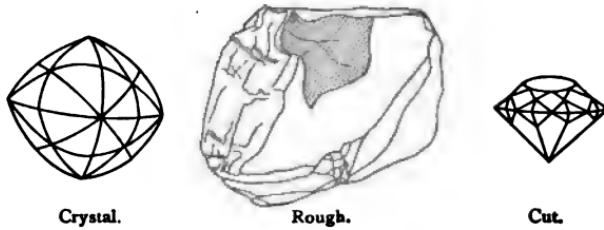


FIG. 24.—Diamonds.

Diamonds have always been prized as gems on account of their beauty, rarity, and permanency. Besides being worn as jewels, they are used to cut glass, and the powder and splinters (known as **bort**) are used to grind and polish diamonds and other hard gems. The impure variety which comes from Brazil, and is called **carbonado**, is set into the end of the "diamond drill," which is used extensively for boring artesian wells and drilling hard rocks.

The diamond was formerly found in gravel deposits in India, and in later years in Brazil. Since 1867, however, about 95 per cent of the diamonds of commerce have come from South Africa. They occur in a bluish volcanic rock along the Vaal River, and especially near Kimberley. Over eight tons of diamonds have been found in South Africa in the last twenty-five years!

The successive investigations of Lavoisier, Dumas, and Davy, extending from 1772 to 1814, showed that diamond is carbon, for when pure diamond was burned in oxygen, the only product was carbon dioxide. This result, which admits of no doubt, has been verified by many famous investigators.

Diamonds have been made by Moissan. He dissolved pure charcoal in melted iron, and poured the molten mass into water. The surface was so suddenly cooled that a tremendous pressure was exerted

FIG. 25.—Artificial diamonds (enlarged) prepared by Moissan.



surface was so suddenly cooled that a tremendous pressure was exerted

by the expanding iron inside the crust. This pressure caused the cooling carbon to crystallize into diamond. The crystals were very small, most of them were black, a few were white, but all had the properties of the diamond (Fig. 25).

The largest diamond thus far known is the Cullinan. It was found in South Africa in 1905, and weighed 3024<sup>1</sup> carats (1.37 lb. avoird.).<sup>1</sup> The cut portions are among the crown jewels of England. Other large cut diamonds are the Orloff (194<sup>1</sup> carats), the Regent (about 136 carats), and the Kohinoor (about 106 carats).

**Graphite** is a soft, black, shiny solid, which is smooth and soapy to the touch. Pure graphite is carbon. It occurs native in large quantities and in many places. One variety is found in abundance at Ticonderoga, New York. Other famous localities are Ceylon, eastern Siberia, Bavaria, and Italy. Sometimes crystals and grains are found, but it usually occurs in flaky masses or slabs. Unlike diamond, graphite is a good conductor of electricity and is often used to coat moulds in electrotyping. It is so soft that it blackens the fingers and leaves a black mark on paper when drawn across it. This property is indicated by the name *graphite*, which is derived from a Greek word (*graphein*) meaning to write. It resembles diamond in its insolubility in liquids at the ordinary temperature. Its specific gravity is 2.2, being considerably lighter than diamond. It produces only carbon dioxide when burned in oxygen; but unlike diamond, it turns into carbon dioxide by heating to a very high temperature in the air. Graphite was once supposed to contain lead, and is even now often incorrectly called "black lead" and plumbago. It is used to make stove polish and protective paints, as a lubricant where oil cannot be used, as the principal ingredient of

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<sup>1</sup> A carat equals 3<sup>1</sup>/<sub>2</sub> Troy grains (or 0.205 gm.). The term is derived from the carob bean, which was used for ages by the diamond merchants of India as a small weight.

graphite crucibles, in which metals are often melted, and in making electrodes for the huge electric furnaces.

Immense quantities of graphite are consumed in the *manufacture of lead pencils*. The graphite is washed free from impurities, ground to a fine powder, mixed with more or less clay, and then pressed through perforated plates, from which the "lead" issues in tiny rods. These are dried, cut into the proper lengths, baked to remove all traces of moisture, and then inserted in the wooden case.

In the United States in 1902 over four million pounds of graphite were mined, and over thirty-two million pounds were imported.

Molten iron and other metals dissolve carbon, and when the metals cool the carbon crystallizes as graphite. Moissan incidentally obtained considerable graphite in making diamonds. Artificial graphite is now manufactured by heating coal in an electric furnace (see Chapter X).

**Amorphous Carbon** is a broad term, including all varieties of coal and charcoal, lampblack, and gas carbon. They are the non-crystalline forms of impure carbon. The word *amorphous* means literally "without form," and it is often used to designate soft, powdery, and uncristallized substances.

Coal is a term applied to several varieties of impure carbon. It may be regarded as the final product derived from vegetable matter which was subjected to heat and pressure through long geological periods.

Ages ago the vegetation was exceedingly dense and luxuriant upon land slightly raised above the sea. In process of time this vegeta-



FIG. 26.—Section of part of the earth's crust near Mauch Chunk, Penn., showing layers of coal.

tion decayed, accumulated, and slowly became covered with sand, mud, and water. The heat of the earth and the enormous pressure of the overlying deposits changed the vegetable matter into more or less

impure carbon. This series of geological and chemical changes was repeated, and as a result we find in the earth layers or seams of carbonaceous matter varying in thickness and composition (Fig. 26). These are the coal beds.

Coal beds contain proofs of their vegetable origin, viz., impressions of vines, stems, and leaves of plants, and similar vegetable substances



FIG. 27.—Fossil found in a coal bed.



FIG. 28.—Section of coal as seen through a microscope.

(Fig. 27). A thin section of coal examined through a microscope reveals a distinct vegetable structure (Fig. 28).

There are three principal kinds of coal. (1) **Bituminous** or soft coal is used to make illuminating gas, coke, and as a fuel for steam; it burns with a smoky flame, and in burning produces much volatile matter. (2) **Anthracite** coal is hard and lustrous. It ignites with difficulty, burns with little or no flame, and produces an intense heat. It is used mainly for domestic purposes,—heating and cooking,—especially in eastern United States. (3) **Lignite** or brown coal is the least valuable as fuel. It often shows the woody fiber and was probably formed much later than the other varieties. **Peat**, strictly speaking, is not coal, though it is used as fuel in some places, especially in Ireland and Holland. It is formed by the slow

decay of roots and other vegetable matter under water, and represents an early stage of coal formation.

The average composition of different kinds of coal is seen by the following table :—

KIND.	CARBON.	VOLATILE MATTER.	ASH.	WATER.
Lignite . . . . .	50.9	20.9	10.2	18
Bituminous . . . . .	74.53	15.13	10.34	—
Anthracite . . . . .	91.64	6.89	1.47	—

Some anthracite coals contain as much as 95 to 99 per cent of carbon, and some bituminous coals as little as 65 per cent. Peat and wood contain still less carbon, but

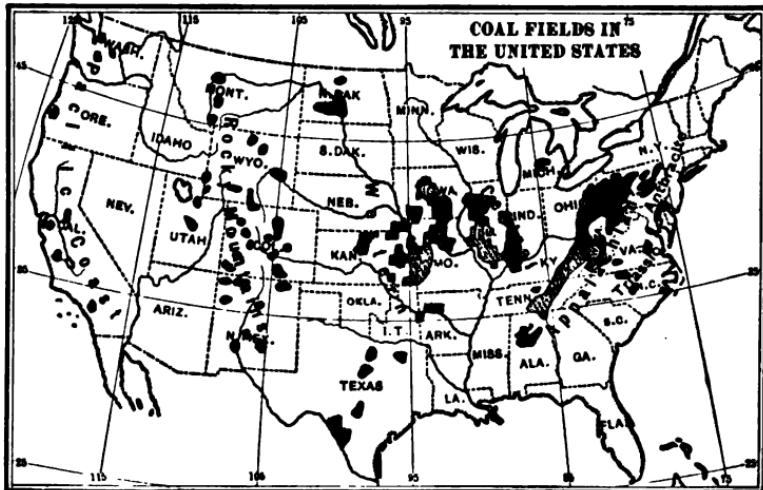


FIG. 29.—Coal fields in the United States.

more volatile matter. The volatile matter includes nitrogen, hydrogen, and sulphur. These facts show that vegetable matter, in passing through the changes which finally

end in coal, loses volatile matter. Anthracite coal, which is found at different depths and associated with rocks of different ages, shows that it was formed from the bituminous variety by the great pressure caused by mountain building. Hence it loses volatile matter and becomes hard.

Coal is widely distributed in the crust of the earth, but the deposits vary in extent and quality. It underlies about one sixth of the area of the United States, the anthracite variety covering less than five hundred square miles in eastern Pennsylvania (Fig. 29). The United States now leads the world in coal production, furnishing about one third of the total supply. England for many years headed the list, and even now furnishes a large amount, for its deposits are extensive (Fig. 30).

**Charcoal** is a variety of amorphous carbon obtained by heating wood, bones, ivory, and other organic matter in closed vessels, or by partially burning them in the air. The process consists essentially in driving off the volatile matter and retaining the carbon.

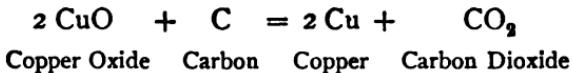
**Wood Charcoal** is a black, brittle solid, and often has the form of the wood from which it is made. It is insoluble, though its mineral impurities may be removed by acids. It burns without flame or much smoke, and leaves a white ash. The compact varieties conduct heat and electricity, but porous charcoal is a poor conductor. It resists the action of many chemicals; hence fence posts, telegraph poles, and wooden piles are often charred before being



FIG. 30.—Coal deposits in the British Isles.

put into the ground. Most varieties are very porous, and when thrown upon water charcoal floats, owing to the presence of air in its pores. Its porosity makes charcoal an excellent absorber of gases, some varieties absorbing ninety times their bulk of ammonia gas. Sewers and foul places are sometimes purified by charcoal. It will also absorb colored substances from solutions. This is especially true of animal charcoal (see below). Foul air and water may be partially purified by charcoal, which forms the essential part of many water filters in houses. Charcoal used for such a purpose, however, must be renewed or often heated to redness; otherwise it becomes clogged and contaminated. Charcoal is never pure carbon, the degree of purity depending upon the kind of wood used, as well as the temperature and method employed.

Besides the uses of charcoal mentioned above, it is used as a fuel, in the manufacture of steel and of gunpowder, and as a medicine. It reduces oxides when heated with them, thus —



Wood charcoal is made either in a charcoal pit or kiln, or in a large retort. Where wood is plentiful, it is loosely piled into the shape shown in Figure 31, and covered with turf to prevent free access of air, though small holes are left at the bottom and a larger one at the top of a central flue, so that sufficient air can pass through the pile. The wood is lighted, and as it slowly burns care is taken to regulate the supply of air, so that the wood will smolder but not burn up. The volatile matter escapes and charcoal remains, the average yield being about 20 per cent of the weight of the wood. This method is crude, uncertain, and wasteful. Much charcoal is now made by heating wood in closed retorts, no air whatever being admitted. By this method, which is called dry or **destructive distillation**, the yield of charcoal is 30 per cent and all the volatile matter is saved. In the

ordinary combustion of wood, the hydrogen forms water and the oxygen forms carbon dioxide; but in dry distillation, where no oxygen is present, much of the hydrogen forms volatile compounds with the carbon and oxygen. Among these volatile products are methyl alcohol

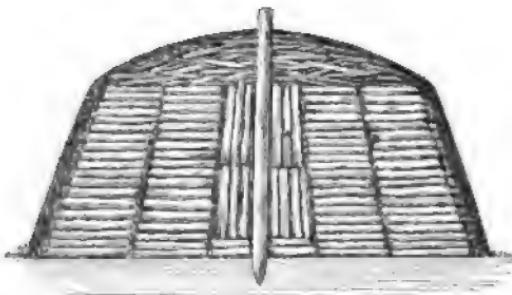


FIG. 31.—Wood arranged for burning into charcoal.

and acetic acid. These are commercial substances, and contribute to the profit of the process. More or less charcoal is obtained by heating any compound of carbon, *e.g.* sugar or starch, the charring being a test for carbon.

**Animal Charcoal or Bone Black** is made by heating bones in a closed vessel, and by heating a mixture of blood and sodium carbonate. It contains only about 10 per cent of carbon, but this carbon is distributed throughout the porous mineral matter of the bone, which is almost entirely calcium phosphate. Under the name of **ivory black**, animal charcoal is used as a pigment, especially in making shoe-blacking. It is extensively used to remove the color from sugar sirups, oils, and other liquids colored by organic matter.

**Coke** is made by expelling the volatile matter from soft coal, somewhat as charcoal is made from wood. It is left in the retorts when coal is distilled in the manufacture of illuminating gas. On a large scale it is made by heating a special grade of soft coal in huge brick ovens, shaped like a beehive, from which air is excluded after combustion begins. Sometimes the coke is made in closed retorts constructed so as to save the by-products,—ammonia, tar,

organic compounds, and combustible gases. This method not only yields more coke, but is also more profitable because the by-products are sold and the combustible gas is used to heat the retorts. Coke is a grayish, porous solid, harder and heavier than charcoal. It burns with no smoke and a feeble flame. It contains about 90 per cent of carbon, the rest being the mineral matter originally in the coal.

Immense quantities of coke are used in the manufacture of iron and steel. It is superior to coal for this purpose, because it gives a greater heat when burned, reduces oxides easily, and contains little or no sulphur or other substances harmful in the iron industries. Coke is the fuel used in making nine tenths of the pig iron in the United States, and over twelve million tons (or about three fourths of the total amount) are made annually in the Connellsville district, near Pittsburgh, Pennsylvania.

**Gas Carbon** is amorphous carbon which is gradually deposited upon the inside of the retorts used in the manufacture of illuminating gas. It is a black, heavy, hard solid, and is almost pure carbon. It is a good conductor of electricity, and is extensively used for the manufacture of the carbon rods of electric lights and for plates of electric batteries.

**Lampblack** is prepared by burning oil or oily substances rich in carbon in a limited supply of air. The dense smoke, which is mainly finely divided carbon, is passed through a series of condensing chambers, where it is collected upon coarse cloth or a cold surface. Its formation is illustrated on a small scale by a smoking lamp, and the soot deposited is the same as lampblack. Lampblack is one of the purest forms of amorphous carbon, and it is used in making printer's ink and certain black paints.

**Allotropism.** — Diamond, graphite, and amorphous carbon, though exhibiting essentially different properties, are identical in composition. All are carbon. They can be changed into one another, the amorphous form into graphite and finally into diamond and the diamond into amorphous carbon. Each burns in oxygen and the product is carbon dioxide. Furthermore, the same weight of each

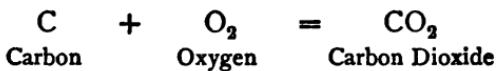
forms the same weight of carbon dioxide, *i.e.* when 12 gm. of each are burned, 44 gm. of carbon dioxide are always produced. There is no doubt about their identity, though no one has explained it. The property of assuming more than one elementary form is called **allotropism** or **allotropy** (from Greek words meaning another form). The more uncommon form is called an **allotrope** or an **allotropic modification** of the other. It is believed by some that allotropism is due to a difference in the number of atoms in a molecule of the element.

#### OXIDES OF CARBON.

**Carbon and Oxygen** do not unite at the ordinary temperature. But when carbon is heated in air, in oxygen, or with some oxides, **carbon dioxide** ( $\text{CO}_2$ ) is formed; if the supply of oxygen is limited, then **carbon monoxide** ( $\text{CO}$ ) is formed.

**Occurrence and Formation of Carbon Dioxide.** — The occurrence of carbon dioxide in the atmosphere and in many natural waters has already been mentioned. It is the main product of ordinary combustion, respiration of animals, and decay. In all these processes the carbon comes from organic matter, while the oxygen comes from the air, from the organic matter, or from both.

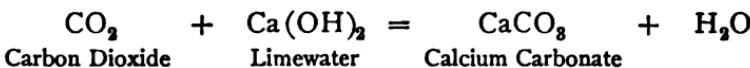
Ordinary combustion is a chemical combining of carbon and oxygen. Hence, when carbon or a substance containing it is burned, carbon dioxide is formed. The equation for this change is —



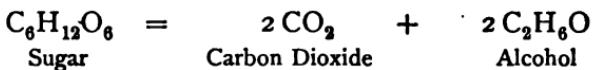
Carbon dioxide is formed by the combustion of such common substances as wood, coal, charcoal, coke, oils, waxes,

cotton, bone, starch, sugar, meat, bread, alcohol, camphor, and illuminating gas.

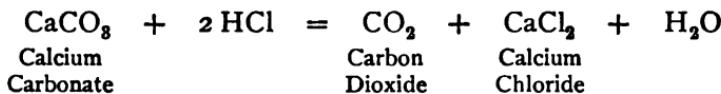
The continuous oxidation of the tissues in the human body produces carbon dioxide (see Relation of Oxygen to Life). And if we exhale the breath through a glass tube into limewater, the carbon dioxide which is in the breath turns the limewater milky—the usual **test for carbon dioxide**. The equation for the change is—



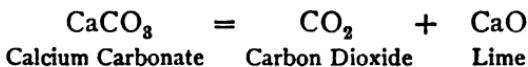
When vegetable and animal matter decays, carbon dioxide is formed. Many kinds of organic matter ferment, especially those containing sugar. By alcoholic fermentation the sugar changes into carbon dioxide and alcohol (see Alcohol), thus—



**The Preparation of Carbon Dioxide** is usually accomplished by the interaction of a carbonate and an acid. Calcium carbonate (limestone or marble) and hydrochloric acid are usually used. The operation may be easily performed in any glass vessel by pouring the acid upon the carbonate. The equation for the chemical change is—



This gas may also be prepared by heating matter containing carbon, or by strongly heating carbonates (as in making lime), thus—

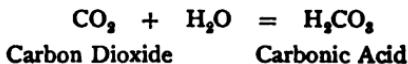


**Properties of Carbon Dioxide.**—This gas has many important properties besides those mentioned under The Atmosphere. It has a slight taste and odor, but no color. It is one and a half times heavier than air, and a liter under standard conditions weighs 1.977 gm. On account of its weight it can be collected by downward displacement and poured from one vessel to another. For the same reason, it is often found at the bottom of old or deep wells, in some valleys near lime kilns or volcanoes, and in mines after explosions. At the ordinary temperature and pressure, water dissolves its own volume of carbon dioxide. Under increased pressure more gas dissolves, which escapes readily when the pressure is removed. Hence "soda water," which is made by forcing carbon dioxide into water, **effervesces** and froths when drawn from the soda fountain. Many natural waters and manufactured beverages (such as champagne and beer) sparkle and effervesce for the same reason. This gas can be readily liquefied by subjecting it to a moderately low temperature. It was first liquefied by Faraday by the method used for chlorine. **Liquid carbon dioxide** is now made in large quantities by forcing the gas into steel cylinders by powerful pumps, the gas being obtained in many cases from the fermenting vats of breweries. When liquid carbon dioxide is allowed to escape into the air, a portion evaporates quickly and thereby withdraws heat from the remainder; if sufficiently cooled, it becomes white, snowlike, solid carbon dioxide. The latter is used to produce low temperatures; a paste of ether and solid carbon dioxide has a temperature of  $-80^{\circ}$  C. Carbon dioxide extinguishes burning objects, such as a blazing stick or lighted candle; indeed, air containing from 2.5 to 4 per cent of carbon dioxide will extinguish

small flames. Hence, the gas is often used to extinguish fires. Many small fire extinguishers contain sodium carbonate and sulphuric acid, so arranged that when desired, carbon dioxide gas may be generated within them under pressure and force a stream of water upon a small blaze, thus often preventing a serious fire. In chemical engines the carbon dioxide, which is similarly generated, forces water from the tank.

**Relation of Carbon Dioxide to Life.**—Animals die when put into carbon dioxide. It cuts off the supply of oxygen as water does from a drowning man. The presence of a small quantity in the air is objectionable, since it is said to produce headache and drowsiness; but much of the discomfort felt in badly ventilated rooms and attributed to carbon dioxide is doubtless due to water vapor and to poisonous substances produced from the organic matter exhaled from the lungs. On the other hand, carbon dioxide is an essential food of plants. Through their leaves and other green parts they absorb carbon dioxide from the atmosphere, decompose it, reject the oxygen, and store up the carbon in the form of starch. The sunlight and the green coloring matter aid the plant in manufacturing its food out of the water (obtained through the roots from the soil) and the carbon of the carbon dioxide obtained from air. Plants thus serve to keep the atmosphere free from an excess of carbon dioxide, the proportion present in the air being very small and practically constant.

**Carbonic Acid.**—Carbon dioxide gas is often called carbonic acid gas, or simply carbonic acid. It is believed that carbon dioxide, when passed into water, combines with the water and forms a weak, unstable acid, which is, strictly speaking, carbonic acid. The equation for this change is—



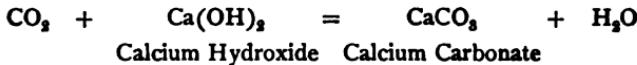
Such a solution reddens blue litmus and decolorizes pink phenolphthalein. Carbonic acid has never been obtained free, and is so unstable that it easily breaks up by gentle heat into carbon dioxide and water, thus —



Carbon dioxide is sometimes called **carbonic anhydride**, to denote its relation to the acid.

**Carbonates** are salts corresponding to the unstable carbonic acid. They are stable compounds. The most abundant natural carbonates are those of calcium, magnesium, and iron. Immense quantities of sodium and potassium carbonates are manufactured.

A few carbonates are formed by direct combination of an oxide and carbon dioxide, but most of them are formed by passing carbon dioxide into the corresponding hydroxide, thus —



Many carbonates are insoluble in water, *e.g.* calcium carbonate, the test for carbon dioxide depending upon this fact. Others, *e.g.* sodium and potassium carbonate, are very soluble. There are two classes of carbonates, the **normal** and the **acid**. Normal sodium carbonate is  $\text{Na}_2\text{CO}_3$ , and acid sodium carbonate is  $\text{HNaCO}_3$ . The latter is often called **sodium bicarbonate**. Normal calcium carbonate is  $\text{CaCO}_3$ , and acid calcium carbonate is  $\text{H}_2\text{Ca}(\text{CO}_3)_2$ ; the latter is unstable, and is easily decomposed by heat into normal calcium carbonate.

**Composition of Carbon Dioxide.**— If a known weight of pure carbon, such as diamond or graphite, is burned in oxygen, it is found that for 12 parts of carbon used there are 44 parts of carbon dioxide formed. Hence 12 parts of carbon unite with 32 parts of oxygen. The vapor density of the gas is 22, and the molecular weight must be 44. These facts necessitate the formula  $\text{CO}_2$ .

**History of Carbon Dioxide.** — This gas was described in the seventeenth century by Van Helmont, who called it *gas sylvestre*. He prepared it by the interaction of acids and carbonates, detected it in mineral water, and observed its formation during combustion and fermentation, as well as its action on animals and flames. Black, in 1755, showed that carbon dioxide is essentially different from ordinary air and that the gas is readily obtained from magnesium and calcium carbonates. Since the gas was combined or "fixed" in these substances, he called the gas fixed air. His work was verified in 1774 by Bergman, who called the gas acid of air. Lavoisier first proved it to be an oxide of carbon.

**Carbon Monoxide** is formed when carbon is burned in a limited supply of air, thus—



If carbon dioxide is passed over heated charcoal, the product is carbon monoxide. That is, carbon reduces carbon dioxide to carbon monoxide, the equation for the change being—

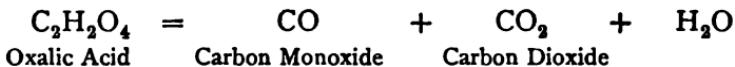


This chemical change takes place in every coal fire. The oxygen of the air entering the bottom of the fire unites with the carbon to form carbon dioxide ; the latter gas in passing through the hot carbon of the fire is reduced to carbon monoxide. Some of the carbon monoxide escapes and some burns with a flickering bluish flame on the top of the fire.

If steam is passed over red-hot coke or charcoal, a mixture of carbon monoxide and hydrogen is produced. This mixture enriched by vapor from oils is known as **water gas** (see Water Gas).

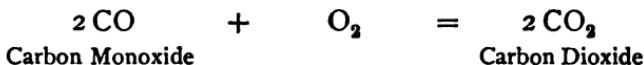
Carbon monoxide is usually prepared by gently heating a mixture of oxalic acid and sulphuric acid in a flask, and

collecting the gaseous product over water. The oxalic acid decomposes thus —

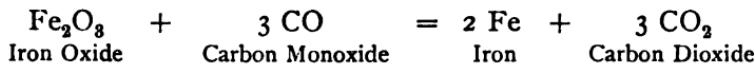


The carbon dioxide may be removed by passing the mixed gases through a solution of sodium hydroxide.

Carbon monoxide is a gas without color, odor, or taste, and is only slightly soluble in water. It burns with a bluish flame, forming carbon dioxide, thus —



Carbon monoxide is extremely poisonous, and it is doubly dangerous because its lack of odor prevents its detection in time to escape its stupefying effect. Many deaths have been caused by breathing air containing it. Carbon monoxide forms a compound with one of the constituents of the blood, and those who have been poisoned by it cannot usually be revived, as in the case of suffocation by carbon dioxide. It is a constituent of ordinary illuminating gas, and care should always be taken to prevent the escape of illuminating gas (as well as the gas from a coal stove or furnace) into rooms occupied by human beings. At a high temperature carbon monoxide readily reduces oxides, and it is, therefore, an important agent in the reduction of iron ores in the blast furnace. This action might be represented thus —



Carbon monoxide, which is sometimes called **carbonic oxide**, forms no acid and therefore no salts. It does not make limewater milky, thus being readily distinguished from carbon dioxide. Its blue flame dis-

tinguishes it from all other gases which burn. It unites directly with chlorine to form carbonyl chloride (phosgene,  $\text{COCl}_2$ ), and with some metals, forming metallic carbonyls, e.g. nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ).

**Cyanogen** is a compound of carbon and nitrogen having the composition corresponding to the formula  $(\text{CN})_2$ . It is a colorless gas; has the odor of peach kernels, is exceedingly poisonous, and burns with a purplish flame. It may be prepared by heating mercuric cyanide ( $\text{Hg}(\text{CN})_2$ ). Cyanogen is a radical, and in compounds it acts like an element. Its corresponding acid is **hydrocyanic** or **prussic acid** (HCN). This acid is prepared by heating a cyanide with sulphuric acid, just as hydrochloric acid is obtained from a chloride. The solution smells like peach kernels, and is one of the most deadly of all known poisons. **Potassium cyanide** (KCN) is a deliquescent solid. It is a deadly poison. Large quantities are used in gold and silver plating and in the "cyanide process" of extracting gold from its ores, as described under that metal. Other cyanogen compounds are **cyanic acid** ( $\text{CNOH}$ ), **sulphocyanic acid** ( $\text{CNSH}$ ), and **potassium sulphocyanate** ( $\text{CNSK}$ ). The last is a white, crystallized salt, which produces a beautiful red solution when added to certain soluble iron compounds, and is therefore used to detect this metal. Salts of complex acids related to hydrocyanic acid are used in dyeing, many being prepared from the most common one—**potassium ferrocyanide** or yellow prussiate of potash. They will be described in the chapter on Iron.

#### **EXERCISES.**

1. What is the symbol and atomic weight of carbon?
2. In what forms does free carbon occur in nature? Name ten familiar solids, three liquids, and two gases containing carbon. What proportion of the earth's crust is carbon?

3. What is diamond? How could the correctness of your answer be shown? State (a) the source, (b) the properties, and (c) the uses of diamonds. Give a brief account of one or more famous diamonds.
4. What is graphite? What is its chemical relation to diamond, and how could this relation be proved? State (a) the source, (b) the properties, and (c) the uses of native graphite.
5. What is (a) black lead, (b) plumbago, (c) bort, (d) carbonado, (e) native graphite, (f) artificial graphite?
6. Give a brief account of the manufacture of lead pencils. What is the literal meaning of graphite?
7. Review artificial graphite (see Chapter X).
8. What does the term *amorphous carbon* include? Does the carbon in these impure forms differ chemically from diamond and graphite?
9. How was coal formed? Give several proofs of its origin. State the properties and uses of (a) bituminous coal, (b) anthracite coal, and (c) lignite. What besides carbon does it contain? Where is coal found?
10. What is charcoal? State (a) the properties, and (b) the uses of wood charcoal. Give a brief account of both methods of preparing wood charcoal. State the preparation, properties, and uses of animal charcoal.
11. What is coke? How is it made? What are its properties? How is it related to the iron industries?
12. What is gas carbon? What is its source? State its properties and uses.
13. What is lampblack? State its method of preparation, properties, and uses.
14. Define and illustrate (a) amorphous, and (b) allotropism.
15. Develop the topics: (a) carbon is a reducing agent, (b) carbon monoxide is a reducing agent, (c) diamond, graphite, and pure amorphous carbon illustrate allotropism.
16. What is (a) hard coal, (b) soft coal, (c) peat, (d) boneblack, (e) soot, (f) lampblack, (g) lignite, (h) electric light carbon?
17. Give the names and formulas of the two oxides of carbon. How is each formed from carbon and oxygen?
18. Describe the occurrence and formation of carbon dioxide. What is always obtained by burning a substance containing carbon? Give the simplest equation for this chemical change.
19. Describe fully the action of carbon dioxide on limewater. Give the equation for the reaction.

20. What is the relation of carbon dioxide to (a) respiration, (b) fermentation of sugar, (c) decay, (d) making lime?
21. What is the test for (a) carbon, (b) carbon monoxide, (c) carbon dioxide?
22. Describe the usual method of preparing carbon dioxide. Give the equation for the reaction. State its properties.
23. Describe liquid and solid carbon dioxide. How are they prepared? For what are they used?
24. What is the relation of carbon dioxide to animal and to plant life?
25. State fully the relation of carbon dioxide to the unstable acid  $H_2CO_3$ . Give the equations for the formation and decomposition of this acid.
26. What are carbonates? Name three. How are they formed? What are their properties?
27. What is (a) "soda water," (b) carbonated water, (c) carbonic acid, (d) carbonic oxide, (e) carbonic anhydride, (f) limestone or marble?
28. What is the difference between (a) sodium carbonate and sodium bicarbonate, and (b) calcium carbonate and acid calcium carbonate?
29. Why is (a)  $CO_2$  the formula of carbon dioxide, and (b)  $CO$  of carbon monoxide?
30. State briefly the history of carbon dioxide.
31. Give a brief account of (a) Black, (b) Van Helmont, and (c) Bergman.
32. Illustrate the law of multiple proportions by the oxides of carbon.
33. Give the equations for (a) the oxidation of carbon to carbon monoxide, (b) the reduction of carbon dioxide to carbon monoxide.
34. How is carbon monoxide (a) formed, and (b) usually prepared?
35. What is the relation of carbon monoxide to water gas?
36. What are the properties of carbon monoxide?
37. Illustrate Gay-Lussac's law by the combustion of carbon monoxide ( $2 CO + O_2 = 2 CO_2$ ).
38. Illuminating gas, water gas, and the gas which escapes from a coal fire are poisonous. Why?
39. What is cyanogen? Hydrocyanic acid? Describe potassium cyanide. For what is it used? Describe potassium sulphocyanate. State its chief use.

40. The specific gravity of charcoal is about 1.5. Why does it float on water?
41. How can carbon monoxide and carbon dioxide be changed into each other?
42. Review (a) combustion, (b) solution of gases (especially carbon dioxide) in water, (c) respiration.
43. State and explain the various chemical changes which occur from the entrance of oxygen (in the air) below the grate of a red-hot coal fire to the end of the burning of the carbon monoxide at the top of the coal.

#### PROBLEMS.

1. How many grams of calcium carbonate are needed to prepare 132 gm. of carbon dioxide?
2. What weight of carbon burned in air will produce 11 gm. of carbon dioxide?
3. Calculate the percentage composition of (a) calcium carbonate, (b) carbon monoxide, (c) carbon dioxide, (d) magnesium carbonate.
4. What per cent of carbon (by weight) is contained in carbon monoxide and in carbon dioxide?
5. If 20 gm. of carbon are heated in the presence of 44 gm. of carbon dioxide, (a) what weight of carbon monoxide is formed, and (b) what weight, if any, of carbon remains?
6. How many liters of carbon dioxide must be passed over red-hot charcoal to yield 84 gm. of carbon monoxide?
7. How much carbon dioxide (a) by weight and (b) by volume is in the air of a room 6 m. long, 4 m. wide, and 3 m. high, if there is 1 vol. of carbon dioxide in 1000 vol. of air?
8. What weight of water must be decomposed to furnish enough oxygen to form (with pure carbon) 44 gm. of carbon dioxide?
9. How many grams of calcium carbonate will produce 15 l. of carbon dioxide?
10. If a piece of pure graphite weighing 7 gm. is burned in oxygen, what volume of carbon dioxide is formed?

## CHAPTER XV.

### **HYDROCARBONS — METHANE — ETHYLENE — ACETYLENE — ILLUMINATING GAS — FLAME — BUNSEN BURNER — OXIDIZING AND REDUCING FLAMES.**

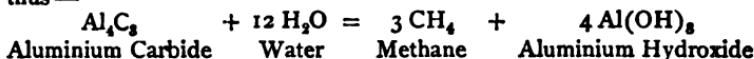
**Hydrocarbons** are compounds of carbon and hydrogen. They number about two hundred, and their properties vary between wide limits. They are found in petroleum and its products (kerosene, naphtha, lubricating oils, paraffin wax, etc.), in coal tar, in coal gas and natural gas, and in some essential oils, such as turpentine. On a large scale they are prepared by the destructive distillation of petroleum, wood, coal, and coal tar. Indirectly the hydrocarbons are the source of many other compounds of carbon, which are extensively used in numerous industries.

The existence of so many hydrocarbons is due to the fact that atoms of carbon have power to unite with themselves. This property gives rise to compounds which form natural groups or series. Simple relations exist between many hydrocarbons, especially between members of the same series. The consecutive members of a series differ in composition by  $\text{CH}_2$ . Thus, in the **methane series**, methane is  $\text{CH}_4$  and ethane is  $\text{C}_2\text{H}_6$ ; in the **ethylene series**, ethylene is  $\text{C}_2\text{H}_4$  and propylene is  $\text{C}_3\text{H}_6$ ; in the **acetylene series**, acetylene is  $\text{C}_2\text{H}_2$  and allylene is  $\text{C}_3\text{H}_4$ ; and in the **benzene series**, benzene is  $\text{C}_6\text{H}_6$  and toluene is  $\text{C}_7\text{H}_8$ . These series are called **homologous series**.

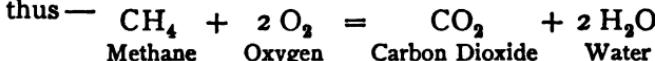
**Methane** is found in coal mines, being a gaseous product of the processes which changed vegetable matter into coal. It is called **fire damp** by miners. It is also formed in marshy places by the decay of vegetable matter under water, and is therefore often called **marsh gas**.

It is a constituent of natural gas and petroleum, and forms a large proportion of the illuminating gas obtained by heating coal.

Methane is usually prepared in the laboratory by heating a mixture of sodium acetate, sodium hydroxide, and quicklime in a hard glass or metal vessel, and collecting the gaseous product over water. It may also be prepared by the interaction of aluminium carbide and water, thus—



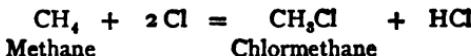
Methane has no color, taste, or odor. It burns with a pale, luminous flame. A mixture of methane with oxygen or air explodes violently when ignited by a spark or flame. Terrible disasters occur in coal mines from this cause. The products of the explosion are carbon dioxide and water,



The carbon dioxide, called **choke damp** or **black damp** by the miners, often suffocates those who escape from the explosion.

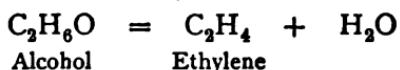
Other members of the methane series are ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), butane ( $C_4H_{10}$ ). This series is also called the **paraffin series**, on account of the chemical indifference of its members. It has the general formula  $C_nH_{2n+2}$ . Butane and the succeeding fifteen or twenty members are liquids, and the highest members are solids.

Chlorine and hydrocarbons interact, that is, chlorine replaces hydrogen, atom for atom. Thus—

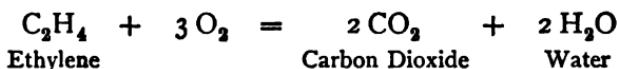


This chemical change is called **substitution**, and illustrates one of the methods used in preparing derivatives of carbon known as **substitution products**. The paraffins are **saturated** hydrocarbons. This means that the carbon in them is saturated, so to speak, with hydrogen, and has no tendency to unite directly with more atoms of hydrogen or other elements.

**Ethylene** or olefiant gas is formed by the destructive distillation of wood and coal. It is usually prepared by heating a mixture of concentrated sulphuric acid and ethyl alcohol, and collecting the gas over water. The alcohol decomposes into ethylene and water, the latter being absorbed by the sulphuric acid. The essential change is represented thus —

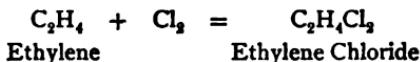


Ethylene is a colorless gas, and has a pleasant odor. It can be condensed to a liquid, which by evaporation produces a temperature as low as  $-140^{\circ}\text{C}$ . It burns with a bright, yellow flame, and is one of the illuminating constituents of coal gas. When ethylene burns, the complete combustion is represented thus —



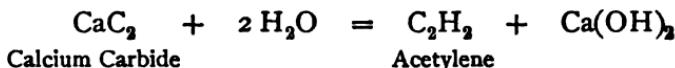
If mixed with oxygen in this proportion and ignited, the mixture explodes.

Other numbers of this series are propylene ( $\text{C}_3\text{H}_6$ ) and butylene ( $\text{C}_4\text{H}_8$ ). These are **unsaturated** hydrocarbons. Unlike the paraffins, they form **addition products** by uniting directly with other substances, especially chlorine, thus —



Ethylene chloride is one of the two dichlorethanes; they have the same percentage composition, molecular weight, and formula ( $\text{C}_2\text{H}_4\text{Cl}_2$ ), but are very different compounds. They illustrate **isomerism** and are called **isomers**. This kind of isomerism is called **metamerism**. The difference in properties is believed to be due to a different arrangement of the atoms in the molecules. Isomerism occurs frequently among carbon compounds.

**Acetylene** is formed by the direct union of hydrogen and carbon when an electric arc is produced between two carbon rods in hydrogen gas. This method of formation, though not convenient, is interesting, because no other hydrocarbon has as yet been directly built up from its elements. A small quantity is present in coal gas. It is also formed by the incomplete combustion of coal gas, e.g. when the flame of a Bunsen burner strikes back and burns at the base (see Bunsen Burner). Acetylene is now prepared cheaply on a large scale by treating calcium carbide with water, thus —



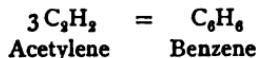
Acetylene is a colorless gas, and, if impure, has an offensive odor. It is poisonous if breathed in large quantities, but much less dangerous than gases containing carbon monoxide. It is lighter than air, its density being about 0.92. Water at the ordinary temperature dissolves its own volume of the gas. Reliable tests show that acetylene does not act upon any common metal or alloy, though it forms explosive compounds with salts of metals, especially copper. As a precaution, copper and brass are seldom used in large vessels containing or generating acetylene, though they might be safely used on small vessels like bicycle lamps.

If acetylene gas is cooled below  $35^{\circ}\text{C}.$ , it can be readily liquefied. Cylinders of liquid acetylene have exploded, causing loss of life and destruction of property, and its use in this form has been prohibited in some localities. Under ordinary atmospheric conditions acetylene will not explode. If compressed, it will explode when a spark or flame is brought near it. A mixture of acetylene and air, if ignited, explodes. The mixture to be explosive, however, must contain a very large per cent of acetylene gas (a condition hardly possible

except from sheer carelessness), because the disagreeable odor reveals the presence of the gas. Acetylene must be used with the same precaution as any other illuminating gas.

Acetylene is found by analysis to contain only carbon and hydrogen combined in the ratio of 12 to 1 by weight. Its vapor density is 13. Therefore its molecular weight must be 26 and its formula  $C_2H_2$ .

Acetylene is an unsaturated hydrocarbon, and like ethylene combines directly with bromine, hydrogen, and other elements. When passed into silver or copper solutions, it forms explosive compounds called acetylides (*e.g.*  $Ag_2C_2$  and  $Cu_2C_2$ ). Heated to a high temperature, it changes into other hydrocarbons, one being benzene, thus—



At a very high temperature (about  $800^{\circ}\text{C}.$ ) it decomposes into carbon and hydrogen. The change of acetylene into benzene illustrates polymerism. Polymers have the same percentage composition, but different molecular weights (see Isomerism).

**Acetylene as an Illuminant.**—Acetylene burns in the air with a luminous, smoky flame. But when air is mixed

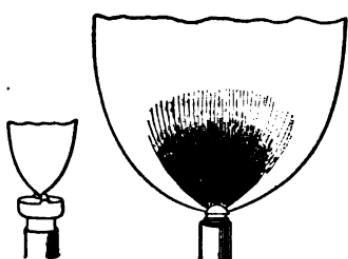


FIG. 32.—Relative size of acetylene and illuminating gas flames giving the same amount of light. The acetylene (smaller) flame consumes only one tenth as much gas an hour as the illuminating gas flame. (One half actual size.)

with the gas as the latter issues from a small opening, the mixture burns with a brilliant, white flame, which does not smoke. It is gradually coming into use as an illuminant. The flame is almost like sunlight, hence by the acetylene flame most colors appear the same as in daylight. It is also adapted for taking photographs, since its action closely resembles

that of the sun. It is a diffusive light, and the flame is much smaller than an ordinary gas flame of the same lighting power (Fig. 32).

With a proper burner the combustion of acetylene is complete, and may be represented thus —

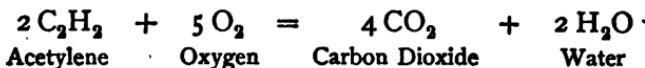


FIG. 33.—Acetylene flame.

In most acetylene burners the gas issues from two small holes drilled at an angle, so that the jets strike each other and produce a flat flame (Fig. 33). Other holes, properly located, permit air to be drawn in mechanically by the acetylene as it rushes through the burner. The openings for the mixture are so fine that the flame cannot strike back and cause an explosion (Fig. 34).



FIG. 34.—Acetylene burner.

**Generation of Acetylene.**—The ease with which acetylene is generated can be shown by putting a little water in a test tube and then dropping in small lumps of calcium carbide. The gas bubbles through the liquid; after the action has proceeded long enough to expel the air, the acetylene may be lighted by holding a burning match at the mouth of the tube. On a larger scale, the gas can be generated by putting the calcium carbide into a flask provided with a dropping funnel and delivery tube, and allowing water to drop slowly upon the carbide; the gas thus generated can be collected in bottles over water. There are two classes of commercial generators. In one, water is added to the calcium carbide, but in the other the carbide drops into the water. The intense heat liberated when calcium carbide interacts with water decomposes acetylene; hence, a generator to be effective and safe should be constructed so that this heat will be absorbed. The first class of generators is dangerous, except when a small quantity of gas is desired, as on the lecture table or in a bicycle lantern. In the second class, a small amount of calcium carbide drops automatically into a large volume of water as fast as the gas is needed, thus insuring a pure, cool gas, and eliminating the danger of an explosion. A pound of calcium carbide yields about five cubic feet of acetylene gas.

**Petroleum** is the source of many useful hydrocarbons. It is an oily liquid obtained from the earth in many parts of the world. In the United States the chief localities are

Ohio, New York, Pennsylvania, West Virginia, Kentucky, Indiana, Colorado, Texas, and California. The immense deposits in Russia are in the Baku district on the Caspian Sea. Some is also found in Canada, India, Japan, and Austria.

Crude petroleum is an oily liquid, with an unpleasant odor. Its color varies from straw to greenish black, and most kinds are greenish in reflected light. It usually floats upon water. Its composition is complex, but all varieties are essentially mixtures of many hydrocarbons. American oils contain chiefly members of the paraffin series. Some varieties contain compounds of nitrogen and of sulphur.

In some localities the oil issues from the earth, but it is usually necessary to drill through rocks and insert a pipe into the porous rock containing oil. At first the oil often "shoots" out of the well in tremendous volumes, owing to the pressure of the confined gas, but after a time a pump is needed to draw it to the surface. The oil is then forced by powerful pumps through large pipes to central points for storage or for delivery to refineries, which are often many miles from the oil well. This network of pipes in the eastern United States is over 25,000 miles long.

Some crude petroleum is used in making water gas (see below), and as fuel on locomotives and steamships, but most of it is separated into various commercial products. This process, which also involves purification, is called refining. The petroleum is distilled in huge iron vessels, and the vapors are condensed as they pass through coiled pipes immersed in cold water. Certain products are obtained from the residue left in the still.

The different distillates, which are collected in separate tanks, are further separated and purified by redistillation. The commercial products obtained from the first distillation are cymogene, rhigolene, gasoline, naphtha, benzine, and kerosene. These liquids are mixtures

of several different hydrocarbons. They are widely used as solvents, fuels, and in making gas.

**Kerosene** is the well-known illuminating oil. Being the most valuable product from petroleum, it is very carefully freed from inflammable liquids and gases, which might cause an explosion, and from tarry matter and semi-solid hydrocarbons, which would clog the wicks of lamps. This is done by agitating it successively with sulphuric acid, sodium hydroxide, and water. Commercial kerosene must have a legal **flashing point**. This is "the temperature at which the oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface." The legal flashing point varies in different localities from 44° to 68° C.

From the residuum left in the still after the first distillation many grades of **lubricating oil**, **vaseline**, and **paraffin wax** are obtained by further treatment. Mineral lubricating oils have largely replaced animal and vegetable oils. Vaseline finds extensive use as an ointment. Paraffin wax is used to make candles, to water-proof paper, to extract oils from plants and flowers, and as a coating for many substances, thereby producing a smooth surface or facilitating slow combustion (as in parlor matches). The final residue is coke. Hydrocarbons are often extracted from it, some is made into electric light carbons, and some is used as a fuel.

This vast industry yields over two hundred different commercial products, many of them being indispensable to the comfort and convenience of mankind. The United States produces annually over 150,000,000 barrels of crude petroleum.

**The Origin of Petroleum** is doubtful. Some think it was produced by the decomposition or slow distillation of plants and animals. Recently it has been suggested that it resulted from the interaction of water and metallic carbides, especially iron carbide, at great depths.

**Natural Gas** is a combustible gas, which issues from the earth in many places. Methane is the principal constituent of the mixture. It is used as a fuel for heating houses, generating steam, and manufacturing iron, steel, glass, brick, and pottery.

In Ohio, Indiana, and other gas-producing regions of the United States, wells, like petroleum wells, are drilled for the escape of natural

gas, which is distributed to consumers through pipes similar to those used for illuminating gas. Enormous quantities are consumed in the United States, the annual product being valued at over \$20,000,000.

**Illuminating Gas.** — Besides acetylene there are other kinds of illuminating gas. Coal gas and water gas are the most common.

**Coal Gas** is made by distilling bituminous coal and purifying the volatile product. The hydrogen in the coal passes off partly as free hydrogen, and partly in combination with carbon as hydrocarbons, and with nitrogen as ammonia. The ammonia, carbon dioxide, and sulphur compounds are regarded as impurities, and are removed before the gas is sent to the consumer. The essential parts of a coal-gas plant are shown in Figure 35.

The coal is distilled in **o-shaped retorts**, made of fire clay and about eight feet long. Six or more retorts are arranged in tiers forming a group or **bench**, so that all the retorts of a bench can be heated by a single fire — usually of coke. Several benches placed end to end constitute a **stack**. The retorts are heated red hot, and about two hundred pounds of coal are evenly distributed on the bottom of each retort with a long iron scoop, and the mouth is quickly and tightly closed by an iron lid. The distillation continues from four to six hours, during which the temperature often reaches  $1200^{\circ}$  C. The lid is then removed, the red-hot coke is pushed or raked out, and another charge of coal is quickly introduced. The coke is quenched with water to prevent further combustion. Some of it is used for heating the retorts, but a part is sold.

The volatile products pass from each retort up through a standpipe, down the dip pipe, and bubble through water into the **hydraulic main**. This is a horizontal, half-round pipe extending the whole length of the stack. Here some of the tar is deposited and ammonium compounds are dissolved by the water which flows constantly through the main. This water is kept at the same level and acts as a "seal" to prevent the gas from passing back into the retorts. The ammoniacal liquor and tar flow into a **tar well**.

From the hydraulic main the gas which is hot and impure passes

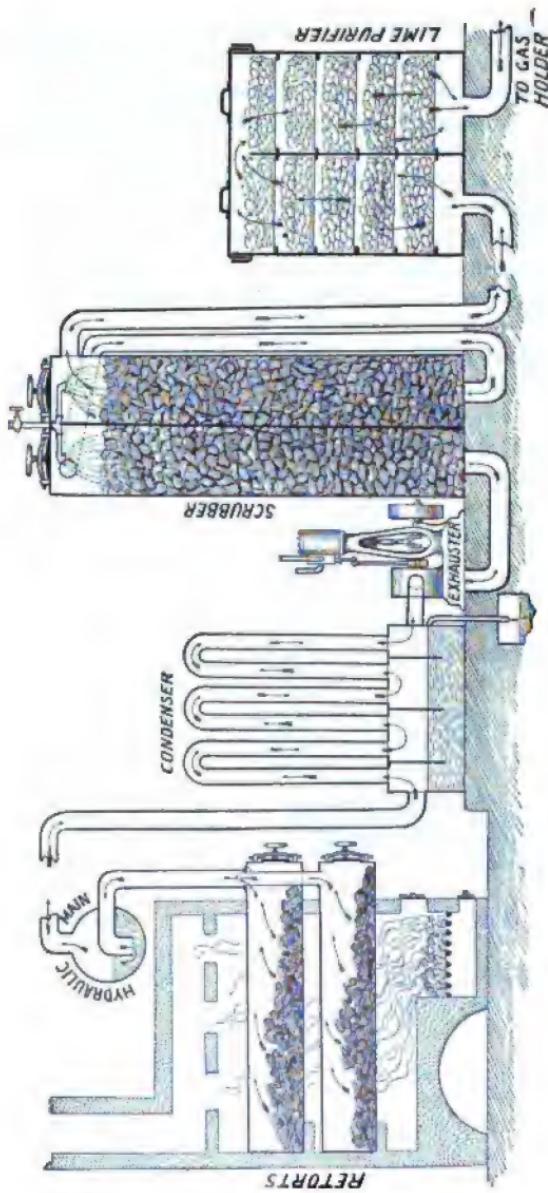


FIG. 35.—Apparatus for manufacturing coal gas.

into the condenser. This is a series of vertical iron pipes, several hundred feet long. They are connected at the top, but they open at the bottom into a series of boxes so constructed that the gas must pass through the entire length of the pipes, while the tar and ammoniacal liquor flow into the tar well. The main object of the condenser is to cool the gas slowly and condense and remove the tar.

An **exhauster**, in most plants, draws or forces the gas from the hydraulic main through the condenser into the scrubber and onward through the purifiers into the gas holder. The exhauster also reduces the pressure in the retorts and regulates the pressure in the holder (see below).

The **scrubber** is a washing machine. Its purpose is to remove the remaining ammonia, part of the carbon dioxide, and hydrogen sulphide gas, and the last traces of tar. Scrubbers vary in construction. One form is a double tower filled with wooden slats or with trays covered with coke or pebbles over which ammoniacal liquor slowly trickles in the first part and pure water in the second. The gas enters at the bottom, meets the descending liquid, and is thoroughly washed. Another form widely used consists of a cylindrical vessel in which numerous wooden slats revolve in compartments and dip into ammoniacal liquor or water at the bottom. The liquid forms a film on the slats and absorbs the ammonia and other gases, while the resulting solution mixes with liquor at the bottom and flows into the proper well. Sometimes a separate **tar extractor** is connected with the scrubber. This is a tower filled with perforated plates, which catch and remove the tar mechanically as the gas passes through into the scrubber.



FIG. 36.—Slat frame (or grid) used in the lime purifier.

low, rectangular iron boxes provided with slat frames loosely covered with lime (Fig. 36). In some plants iron oxide is used as the purifying material.

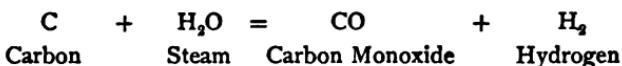
The purified gas next passes through a large **meter**, which records its volume, into a **gas holder**. The holder is an enormous, cylindrical, iron tank in which the gas is stored. It floats in a cistern of water, and rises or falls as the gas enters or leaves. Weights and the pressure

from the exhauster so balance it that it exerts just enough pressure to force the gas through the pipes to the consumer.

A ton of good coal yields about 10,000 cubic feet of gas, 1400 pounds of coke, 120 pounds of tar, 20 gallons of ammoniacal liquor, and a varying amount of gas carbon. The coke is a valuable fuel and finds a ready sale. The tar, or coal tar as it is often called, collected from the hydraulic main and condenser, is a thick, black, foul-smelling liquid. It was formerly thrown away. Some is used for preserving timber, making tarred paper and concrete, and as a protective paint. Most of it is now separated by distillation into its more important constituents, especially benzene ( $C_6H_6$ ). These carbon compounds and their numerous derivatives appear in commerce as oils, medicines, dyestuffs, flavors, perfumes, and other useful products. The ammoniacal liquor from the hydraulic main, condenser, and scrubber is the source of ammonia and its compounds. Gas carbon is the hard deposit which collects on the inside of the retort, and is used in the electrical industries (see Gas Carbon). The sale of these by-products reduces the cost of making the coal gas.

**Water Gas** is made by forcing steam through a mass of red-hot coal and mixing the gaseous product with hot gases obtained from oil. The essential parts of the apparatus are shown in Figure 37.

Air is forced through the coal fire in the generator, and the hot gases which are produced pass down the carbureter, up into the superheater, and escape through its top into the open air. This operation lasts about four minutes, and is called the "blow." It heats the fire brick inside the carburetor and superheater intensely hot, air often being forced in to raise the temperature. The air valves and the top of the superheater are now closed, and the "run" begins, which lasts about six minutes. Steam is forced into the generator at the bottom. In passing through the mass of incandescent carbon the steam and carbon interact thus —



This mixture of hydrogen and carbon monoxide burns with a feeble flame, and before it can be used as an illuminating gas it must be

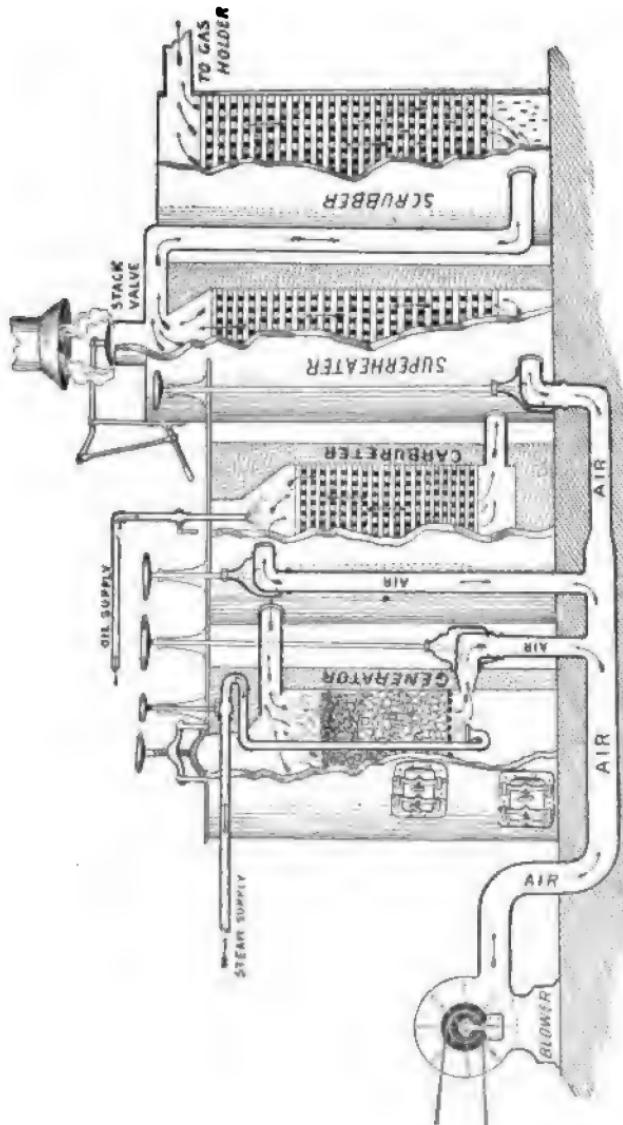


FIG. 37.—Apparatus for manufacturing water gas. In many plants a seal box (similar to the seal in the hydraulic main) is placed between the superheater and scrubber to prevent the backward flow of the gas.

enriched with gases which are illuminants. Therefore, the mixed gases pass to the top of the carburetor, where they meet a spray of oil. And as the gaseous mixture passes down the carburetor and up the superheater, the hydrocarbons of the oil are transformed by the intense heat into hydrocarbons that do not liquefy when the gas is cooled. The addition of hydrocarbons is called **carbureting**. From the superheater the water gas passes through the purifying apparatus into a holder.

Water gas is seldom burned alone, but is usually mixed with 60 or 70 per cent of coal gas. This mixture is popularly called "illuminating gas." Owing to the high percentage of carbon monoxide, water gas and gases containing it are **poisonous**.

**Characteristics of Illuminating Gases.** — Both coal gas and water gas have a disagreeable odor. They are mixtures having a composition which varies with the coal used, the temperature reached, and the degree of purification attained. The following table shows the average —

#### COMPOSITION OF ILLUMINATING GASES.

CONSTITUENTS.	COAL GAS.	WATER GAS.
Marsh gas . . . . .	34.5	19.8
Ethylene (and other illuminants)	5.0	16.6
Hydrogen . . . . .	49.0	32.1
Carbon monoxide . . . . .	7.2	26.1
Carbon dioxide . . . . .	1.1	3.0
Nitrogen . . . . .	3.2	2.4

Both kinds of illuminating gas may contain a little oxygen, and traces of ammonia and hydrogen sulphide gases. Nitrogen and the last portions of carbon dioxide are impurities not easily removed. Marsh gas, hydrogen, and carbon monoxide burn with a feeble (non-yellow) flame, and are often called **diluents**; they furnish heat, but no light.

The **luminosity** of illuminating gas depends mainly upon the presence of hydrocarbons containing a relatively large proportion of carbon. Acetylene gas, which gives such a brilliant light, consists almost wholly of this hydrocarbon containing 90 per cent of carbon. The most important **illuminants** in coal gas and water gas are ethylene and similar hydrocarbons, acetylene, and benzene ( $C_6H_6$ ).

The commercial value of an illuminating gas depends upon its **illuminating power**. This property is measured by a photometer and is expressed in "candles." The determination is made by comparing the light produced by burning the gas in a standard burner at the rate of five cubic feet an hour with the light produced by a standard wax candle burning at the rate of 120 grains (7.77 gm.) an hour. If the gas flame is 20 times brighter than the candle flame, then the candle power of the gas is 20. The candle power of ordinary coal gas is about 17, and that of water gas is about 25. Ordinary illuminating gas has a candle power of about 20, since it is usually a mixture of coal gas and water gas.

**Flame.**—A flame is a mass of burning gas. Ordinarily it is gas combining chemically with the oxygen of the air. In the illuminating gas flame the gas itself is burning in the air. In a lamp flame the gas which burns comes from the oil which is drawn up the wick by capillary attraction, and then volatilized by the heat. Similarly, in a candle flame the burning gas comes from the melted wax. The flame produced by most burning hydrocarbons is yellowish white.

The hydrocarbon flame has several distinct parts, though the structure of the flame is essentially the same, whether produced by burning illuminating gas, kerosene oil, or candle wax. The candle flame may be taken as the type. An examination of the enlarged vertical section shown in Figure 38 reveals four somewhat conical portions. (1) Around the wick there is a black cone (*A*), filled with combustible

gases formed from the melted wax. They do not burn because no oxygen is present. With a glass tube of fine bore it is possible to draw off these gases from a large flame and light them at the upper end of the tube. (2) Around the lower part of the dark cone is a faint bluish cup-shaped part (*B, B*). It is the lower portion of the exterior cone where complete combustion of the gases occurs, since plenty of oxygen from the air reaches this portion. (3) Above the dark cone is the luminous portion (*C*). It is the largest and most important part of the flame. It is popularly spoken of as "the flame." Combustion is incomplete here, because little or no oxygen can pass through the exterior cone. The temperature is high, however, and the hydrocarbons undergo complex changes. Acetylene is probably formed. The most characteristic change is the liberation of small particles of carbon. This liberated carbon heated to incandescence by the burning gases makes the flame luminous. The carbon glows but does not burn up, because little or no oxygen is present. A crayon or glass rod held in this part of the flame is at once coated with soot, which consists of fine particles of carbon. (4) The exterior cone (*D, D*) is almost invisible. Here combustion is complete, because the oxygen of the air changes all the carbon into carbon dioxide.

That this is the hottest region may be easily shown by pressing a piece of stiff white paper for an instant down upon the flame almost to the wick. The paper will be charred by the outer part of the flame, as shown in Figure 39.



FIG. 39.—Paper charred by a candle flame.

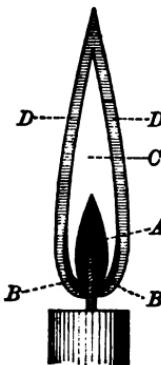


FIG. 38.—Candle flame.

These four portions may be found in all luminous hydrocarbon flames, whatever the shape. An ordinary gas flame is flattened by forcing the gas flame through a narrow slit in the burner, so that the flame will give more light. The blue part is easily seen, however, when the gas flame is turned low or looked at through a small opening; the dark and yellow parts are always visible—the latter being intentionally enlarged. The flat or circular flame of an oil lamp likewise presents the same characteristics.

The gaseous products of the combustion of hydrocarbons are water vapor and carbon dioxide. A bottle in which a candle is burning has, at first, a deposit of moisture on the inside; and if the candle is removed and limewater added, the presence of carbon dioxide is shown by the milkiness of the limewater. The oxygen needed by the burning hydrocarbons is obtained from the air. If not enough oxygen is present, the flame smokes, *i.e.* the carbon is thrown off into the air before the particles are heated hot enough to glow. All oil lamps are so constructed that air enters the burner below the flame. Large oil lamps have a central opening through which a large volume of air passes up inside the circular flame. Otherwise the lamp would burn with a very smoky flame.

The luminosity of hydrocarbon flames is affected by other things besides the presence of glowing carbon. One of these is temperature. Gases cooled before being burned give poor light. A candle flame may be cooled enough to extinguish it. Thus, if a coil of copper wire is lowered upon a candle flame, the flame smokes, loses its yellow color, and finally goes out; but if a coil of hot wire is used, the flame burns unchanged. Gases, as well as solids and liquids, have a **kindling temperature**, *i.e.* a temperature to which they must be heated before they "catch fire." This temperature differs with different substances. As we lower the temperature of gases burning with a luminous flame, their luminosity decreases, and below their kindling point they will not burn. The density of the gases in the flame and of the atmosphere itself likewise modifies luminosity. A candle flame was found by experiment to be smaller on the top of Mont Blanc than at the base.

Not all flames are luminous. The hydrogen flame is almost invisible, and the flames of carbon monoxide and methane are a faint blue. These flames yield no solid particles of carbon, but only gaseous products. The most common non-luminous flame is the Bunsen flame.

**The Bunsen Burner and its Flame.** — When illuminating gas is mixed with air before burning, and the mixture burned in a suitable burner, a flame is produced which is non-luminous and very hot. The temperature of the hottest part is about  $1500^{\circ}\text{C}$ . This flame deposits no carbon, since its products are entirely gaseous. Such a flame is called the **Bunsen flame**, because it is produced in a burner devised by the German chemist Bunsen. This burner is constantly used in chemical laboratories as a source of heat, and modified forms have numerous uses. One form, for example, furnishes the heat in the gas range used for cooking. The parts of an ordinary Bunsen burner are shown in Figure 40. The gas enters the base and escapes through a very small opening into the long tube, which screws down upon this opening. At the lower end of the long tube there are two holes, through which air is drawn by the gas as it rushes out of the small opening. The gas and air mix as they rise in the tube, and this mixture of air and gas burns at the top of the long tube. The size of the air holes at the bottom of the long tube may be changed by a movable ring, thus

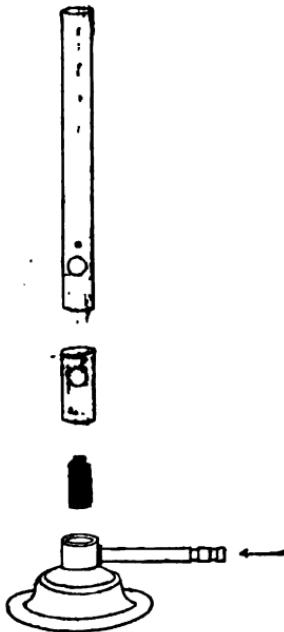


FIG. 40.—Parts of a Bunsen burner.

varying the volume of the entering air. When the holes are open, the typical colorless, hot Bunsen flame is formed. The combustion of the hydrocarbons is practically complete. They burn up before particles of carbon are liberated, thus making the flame non-luminous and free from soot. Apparatus heated by this flame is not blackened. The Bunsen flame may be made momentarily luminous by shaking or blowing fine particles into the flame,—such as powdered charcoal dust, finely divided metals, and sodium compounds.

It was formerly believed that the non-luminous character of the Bunsen flame is solely due to the complete combustion of the carbon by the oxygen of the entering air. Recent experiments have shown, however, that the result is partly due to the diluting action of the nitrogen. The gas burns at top of the tube and not inside, because the proper mixture of gas and air flows out more quickly than the flame can travel back. If the gas supply is slowly decreased, the flame becomes smaller and finally disappears with a slight explosion. This change is called "striking back." It is due to the fact that the tube contains an explosive mixture of air and illuminating gas, through which the flame travels faster than the mixture escapes from the tube. This explosion illustrates in a small way what often happens when a mixture of air and illuminating gas is ignited. Sometimes the flame is not extinguished, but burns within (and sometimes without) the tube. This flame has a pale color, a disagreeable odor, and deposits soot.

The Bunsen flame has many characteristic properties. Its color is bluish, and the different cones have different colors. There are really three cones: (1) the blue or greenish inner one of unburned gases; (2) the very faint blue middle one; (3) and the outer one, which is pale blue, and represents the blue cone in the candle flame. The middle and outer cones are not always easily distinguished; and for all practical purposes it is convenient to divide the flame into two parts,—an **inner cone** of unburned gases

and an **outer cone** in which all the carbon is consumed. Combustible gases may be drawn off by a tube from the inner cone and ignited. A match laid for an instant across the top of the tube is charred only at the two points where it touches the outer cone; and a sulphur match suspended by a pin across the top of an unlighted burner is not kindled when the gas is first lighted. A

piece of wire gauze pressed down upon the flame shows a dark central portion surrounded by a luminous ring. The flame is beneath the gauze, although the gas passes freely through it and escapes. If the gas is extinguished and then relighted above the gauze, it will burn above but not beneath (Fig. 41). The gauze cools the gas below its kindling temperature.

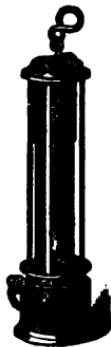


FIG. 42.—One form of Davy's safety lamp.

The miner's safety lamp invented by Davy depends upon this last principle. It is an oil lamp surrounded by a cylinder of fine wire gauze (Fig. 42). When taken into a mine where there are explosive gases (fire damp), the flame continues to burn inside, though its size and color change. The gas often enters the lamp and burns inside, but the flame within does not ignite the gases without because the wire gauze keeps them cooled below their kindling temperature. Hence an explosion is often prevented. When miners notice changes in the lamp flame, they usually seek a safe place.

**Oxidizing and Reducing Flames.**—The outer portion of the Bunsen flame is called the **oxidizing flame**, because here the oxygen is freely given to sub-

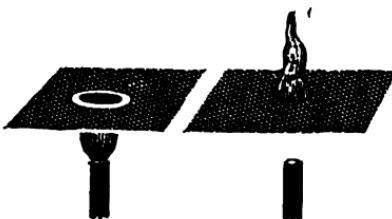


FIG. 41.—The effects of wire gauze on a Bunsen flame.

stances. The inner portion is called the **reducing flame**, because here the hydrocarbons withdraw oxygen. A sketch of the general relation of these flames is shown in Figure 43. *A* is the most effective part of the oxidizing flame, and *B* of the reducing flame. At *A* metals are oxidized, and at *B* oxygen compounds are reduced.



FIG. 43.—The oxidizing (*A*) and reducing (*B*) flames.

Sometimes a long tube with a small opening at one end, called a **blowpipe**, is used to produce these flames. A tube with a flattened top is put inside the burner tube to produce a luminous flame. The tip of the blowpipe rests in or near this flame, and if air is gently and continuously blown through the blowpipe, a long, slender flame is produced, called a **blowpipe flame** (Fig. 44). It is like the Bunsen flame as far as its oxidizing and reducing

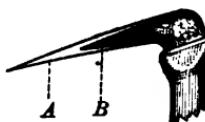


FIG. 44.—Blowpipe flame, showing oxidizing (*A*) and reducing (*B*) parts.

properties are concerned. The blowpipe is used in the laboratory and by jewelers and mineralogists. On a large scale the blowpipe flame is used to reduce or oxidize ores and to melt refractory substances (see Compound Blowpipe).

The Bunsen flame has recently been utilized in producing the **Welsbach light**. The non-luminous flame heats a conical mantle of oxides of thorium and cerium, and the mantle glows with an intense light. The candle power varies from 40 to 100. This form of burner is widely used because it produces a brilliant light.

### **EXERCISES.**

1. What are hydrocarbons? Where are they found? Name several familiar substances containing hydrocarbons.
2. Are there many hydrocarbons? Why?
3. What is an homologous series of hydrocarbons? Name four such series.

4. What is methane? What other names has it? Where is it found? How is it usually prepared? State its essential properties. Why is it a dangerous gas? Illustrate your answer by an equation.
5. What other name has the methane series? Why? Illustrate the following terms by the paraffin series: (a) substitution, (b) substitution product, (c) saturated hydrocarbon.
6. What is ethylene? How is it prepared? Where is it found? State its properties. Give the equation expressing the combustion of ethylene.
7. Illustrate the following terms by the ethylene series: (a) unsaturated hydrocarbon, (b) addition product, (c) isomerism, (d) metamerism, (e) isomer.
8. Review the subject of calcium carbide (see Chapter X).
9. What is acetylene? How is it formed? How is it prepared? Give the equation for the reaction. Summarize the properties of acetylene.
10. Illustrate the following terms by acetylene: (a) polymerism, (b) polymer, (c) unsaturated hydrocarbon.
11. Describe the acetylene (a) flame, (b) burner, and (c) generator. What precautions must be observed in using acetylene as an illuminant?
12. What is (a) choke damp, (b) black damp, (c) marsh gas, (d) olefiant gas?
13. What is the formula of (a) methane, (b) ethylene, (c) benzene? Why is  $C_2H_2$  the formula of acetylene?
14. How many volumes of oxygen are needed for the combustion of one volume of (a) methane, (b) ethylene, and (c) of two volumes of acetylene? What volumes of what products are formed in each case? What law do these relations illustrate?
15. What is petroleum? Where is it found? Of what is petroleum composed? How is it obtained from the earth? Describe briefly the refining of petroleum.
16. What is kerosene? Describe its method of preparation. Define and illustrate the term *flashing point*.
17. State the uses of (a) gasoline, (b) lubricating oils, (c) vaseline, (d) paraffin wax.
18. What is natural gas? Where is it found? Of what is it composed? For what is it used?
19. What is coal gas? Describe briefly its manufacture.
20. What is coal tar? What are its uses?

21. What is ammoniacal liquor? What is its source? How is it obtained? For what is it used?
22. Review (a) coke, and (b) gas carbon (see Chapter XIV).
23. What is water gas? Describe briefly its manufacture. What is meant by "enriching" water gas? What is producer gas?
24. Give the equation for the interaction of carbon and steam. How many volumes of steam are needed to produce one volume of each of the products?
25. What is illuminating gas? State its chief properties. What are its (a) light-giving constituents, (b) diluents, (c) impurities? Upon what does its luminosity depend? How is this property measured and expressed? Give two reasons why illuminating gas is dangerous.
26. What is a flame? Illustrate your answer. Describe the structure of a candle flame. What are the chief gaseous products of combustion? Why do lamps sometimes smoke? What affects the luminosity of many flames?
27. Describe (a) the Bunsen flame, (b) the Bunsen burner. Why is the Bunsen flame non-luminous? Describe and explain the "striking back" of the Bunsen flame. Describe the structure of the Bunsen flame. What is the miner's safety lamp, and upon what principle is it constructed?
28. Review oxidation and reduction.
29. What is (a) an oxidizing flame? Describe a blowpipe and its flame. For what is it used?
30. Describe the Welsbach light.

#### PROBLEMS.

1. Calculate the percentage composition of (a) methane ( $\text{CH}_4$ ), (b) ethylene ( $\text{C}_2\text{H}_4$ ), and (c) acetylene ( $\text{C}_2\text{H}_2$ ).
2. What weight of oxygen is needed for the complete combustion of 4 gm. of ethylene? (Equation is  $\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$ .)
3. What is the simplest formula of a compound having the composition H = 7.69 and C = 92.3?
4. Calculate the molecular formula of a compound having the vapor density 38.8 and the composition C = 92.3 and H = 7.69.

## CHAPTER XVI.

### FLUORINE — BROMINE — IODINE.

**FLUORINE**, bromine, and iodine, together with chlorine, are often grouped, and called the **halogens**. They resemble each other in a general way, and form analogous compounds which have similar properties, differing mainly in degree.

Halogen means "a sea-salt producer." It is applied to this group of elements because they form salts which resemble sodium chloride (common salt or sea salt). Chlorides, bromides, and iodides are sometimes called haloid salts or **halides**. The Greek word for salt, *hals*, suggested these terms.

#### FLUORINE.

**Occurrence.** — Fluorine is the most active of all the elements, and is therefore never found free in nature. It occurs abundantly in combination with calcium as fluor spar or calcium fluoride ( $\text{CaF}_2$ ). Other native compounds are cryolite ( $\text{Na}_3\text{AlF}_6$ ) and apatite ( $\text{CaF}_2 \cdot 3 \text{Ca}_3(\text{PO}_4)_2$ ). Minute quantities of combined fluorine are found in bones and blood, in the enamel of the teeth, and in sea and some mineral waters.

Fluorine is named from fluor spar, which melts easily and is used as a flux to make substances flow together (hence the derivation from the Latin *fluo*, I flow).

**The Isolation of Fluorine** was accomplished in 1886 by Moissan, though many unsuccessful attempts had been previously made. He decomposed hydrofluoric acid by

electricity and collected the liberated fluorine. The achievement was attended with tremendous difficulties, owing to the intense activity of fluorine and its corrosive properties.

The essential parts of the apparatus used by Moissan are shown in Figure 45. The U-tube, made of an alloy of platinum and iridium, is pro-

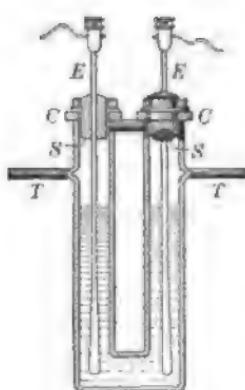


FIG. 45.—Moissan's apparatus for preparing fluorine.

vided with tightly fitting stoppers of fluor spar (*S*, *S*). Through the stoppers pass the electrodes (*E*, *E*) of platinum iridium, held in place by screw caps (*C*, *C*). Side tubes (*T*, *T*) allow the liberated gases (fluorine and hydrogen) to be drawn off separately through platinum delivery tubes. Perfectly dry hydrofluoric acid is put into the U-tube and dry acid potassium fluoride ( $\text{HKF}_3$ ) is added to enable the solution to conduct the current—liquid hydrofluoric acid itself being a non-conductor. The U-tube is cooled to a very low temperature ( $-23^\circ$  to  $-50^\circ \text{ C}.$ ), and on passing a current through the apparatus fluorine is evolved at the positive electrode and hydrogen at the other. The fluorine, freed from hydrofluoric acid vapor, was collected by Moissan

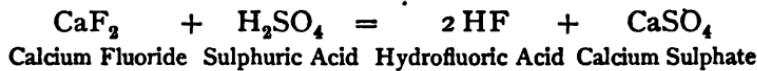
at first in a platinum tube with thin fluor spar plates closing each end, so that he could look inside and examine the gas. Later he found that dry fluorine can be collected in glass tubes, since it attacks glass only very slowly.

**Properties.**—Fluorine has a sharp odor and a greenish yellow color, but lighter and more yellowish than chlorine. Its density is 1.265 (air = 1). Subjected to pressure and a sufficiently low temperature, it becomes a pale yellow liquid, which boils at  $-187^\circ \text{ C}.$  The pure gas can be liquefied in a glass vessel. Chemically, fluorine is intensely active. Hydrogen, bromine, iodine, sulphur, phosphorus, carbon, silicon, and boron take fire in it. Oxygen, nitrogen, and argon do not unite with it. Most metals burn in it, form-

ing fluorides. Gold and platinum are not attacked by it below red heat. Copper becomes coated with copper fluoride, which protects the metal, so that copper vessels may be used as fluorine generators. Moissan used a copper U-tube to prepare large volumes. Water is decomposed by it at ordinary temperatures, owing to the intense attraction between hydrogen and fluorine; hydrocarbons, for a similar reason, are instantly decomposed, hydrofluoric acid and carbon fluorides being the products.

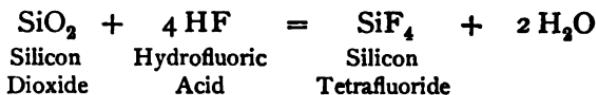
The vapor density of fluorine shows that its molecular weight is about 38; since the atomic weight is 19, each molecule contains two atoms and the formula is  $F_2$ .

**Hydrofluoric Acid**, HF, is the compound of fluorine corresponding to hydrochloric acid. It is prepared by the interaction of a fluoride and concentrated sulphuric acid. Calcium fluoride is usually used, and the experiment is performed in a lead dish. The chemical change is represented thus—



Hydrofluoric acid, like hydrochloric acid, is a colorless gas, which fumes in the air and dissolves in water, the solution being the commercial hydrofluoric acid. Both gas and liquid are dangerous substances. The gas is extremely poisonous, and the liquid, if dropped on the skin, produces terrible sores. Owing to its corrosive action the acid is preserved and sold in platinum, rubber, or wax bottles. The acid and the moist gas attack glass, and are used extensively in **etching**. The glass is coated with wax, and the design to be etched is scratched through the wax. The glass is then exposed to the gas or the liquid, which attacks the exposed places. When the

wax is removed, a permanent etching like the design is visible. Glass is an artificial compound of silicon—a silicate. The corrosive action of hydrofluoric acid upon glass is due to the ease with which the acid decomposes glass and forms with the silicon a volatile compound, called silicon tetrafluoride ( $\text{SiF}_4$ ). Since silicon dioxide (or sand) is the essential constituent of the mixture from which glass is made, the equation for etching glass may be written thus—



Scales on thermometers and on other graduated glass instruments are etched with hydrofluoric acid.

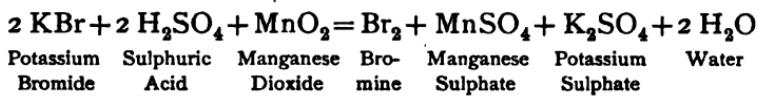
The vapor density of hydrofluoric acid gas indicates that its formula is HF at high temperature, but  $\text{H}_2\text{F}_2$  at lower temperatures ( $30^\circ \text{ C.}$ ).

#### BROMINE.

**Occurrence.**—Bromine is never found free in nature on account of its chemical activity. Bromides are widely distributed, especially magnesium bromide. The salt springs of Ohio, West Virginia, Pennsylvania, and Michigan, and the salt deposits at Stassfurt in Germany furnish the main supply of the element. Sea water, Chili salt-peter ( $\text{NaNO}_3$ ), and certain seaweeds contain a small quantity of combined bromine.

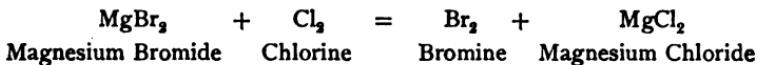
**Preparation.**—Bromine is obtained from its compounds by treatment with chlorine, or with sulphuric acid and manganese dioxide. In the laboratory, bromine is prepared by heating potassium bromide with manganese dioxide and sulphuric acid in a glass vessel. The bromine is easily liberated as a dense, brown vapor, which often

condenses to a liquid and runs down the walls of the vessel. The chemical change is represented thus—



Bromine is sometimes prepared by treating a bromide with manganese dioxide and hydrochloric acid.

The source of commercial bromine in the United States is "bittern"—a concentrated liquid left after salt is crystallized from brine. In the **continuous process** the hot bittern flows down a large tower filled with broken brick or burned clay balls; chlorine gas and steam forced in at the bottom meet the bittern and liberate the bromine, which passes as a vapor out of the top into a condenser. The main chemical change is represented thus—



In the **periodic process**, used chiefly in the United States, a huge stone still is charged with manganese dioxide, hot bittern, and sulphuric acid, and heated by steam. The bromine distills into a condenser, as in the other process. Sometimes potassium chlorate is used as the oxidizing agent.

**Properties.**—Bromine is a heavy, reddish brown liquid at the ordinary temperature. Its specific gravity is about three. It is a volatile liquid, boiling at about 59° C. The vapor, which is given off freely, has a disagreeable, suffocating odor. This property suggested the name *bromine* (from the Greek word *bromos*, a stench). It is poisonous, and burns the flesh frightfully. Bromine is somewhat soluble in water. The solution, called **bromine water**, has a brown color, and when cooled deposits a crystalline hydrate ( $\text{Br}_2 \cdot 10 \text{H}_2\text{O}$ ). Many other properties of bromine are similar to those of chlorine. Thus, it combines with metals and other elements; it also bleaches.

**Compounds of Bromine** are similar to those of chlorine. **Hydrobromic acid** ( $HBr$ ) is a colorless, pungent gas, which fumes in the air and dissolves freely in water, forming the solution usually called hydrobromic acid. Its other properties closely resemble those of hydrochloric acid. **Bromides** are salts of hydrobromic acid, though many are formed by direct combination with bromine. Like the chlorides, most bromides dissolve in water. **Potassium bromide** ( $KBr$ ) is a white solid, made by decomposing iron bromide with potassium carbonate. It is used extensively as a medicine and in photography (in preparing silver bromide plates and films). Bromides of sodium, ammonium, and cadmium have a limited use.

**Miscellaneous.**—Bromine itself is used to make potassium bromide and other compounds, especially a class of coal tar dyes used to color pink string and to make red ink. Annually over 500,000 pounds of bromine are prepared in the United States, while Germany exports about 400,000 pounds of bromine, and 500,000 pounds of bromine compounds.

Balard discovered bromine in 1826 in the mother liquor (or bittern) from brine. Liebig supposed it was chloride of iodine, and thus failed to discover it, because, as he said, he yielded to "explanations not founded on experiment."

#### IODINE.

**Occurrence.**—Free iodine is never found in nature, but like chlorine and bromine it is combined with metals, especially sodium, potassium, or magnesium. It is widely distributed, though the quantity in any one place is small. Tobacco, water cress, cod-liver oil, oysters, and sponges contain minute quantities. Native iodides of silver and of mercury are found. The ash of some seaweeds contains from 0.5 to 1.5 per cent of its weight of iodides of sodium and potassium. Sodium iodate ( $NaIO_3$ ) occurs in the deposits of saltpeter in Chili, and is the main source of the element.

**Preparation.**—Iodine is prepared in the laboratory by a method similar to that used for bromine. Potassium iodide, manganese dioxide, and sulphuric acid are heated in a glass vessel, and the iodine appears as a violet vapor, which con-

denses on the upper part of the vessel into dark grayish crystals.

On a commercial scale iodine is prepared from the ash of seaweeds and from the mother liquors of Chili saltpeter. (1) Along the coasts of France, Scotland, and Norway seaweed is collected and burned, usually in closed vessels. The ash is called *kelp* or *varec*. The soluble portions are removed by agitation with water. The filtered liquid is further purified, and from the final mother liquor in which the iodides are dissolved, the iodine is extracted by heating with sulphuric acid and manganese dioxide. Sometimes chlorine is used to extract the iodine. In either case the mother liquor and its added ingredients are distilled

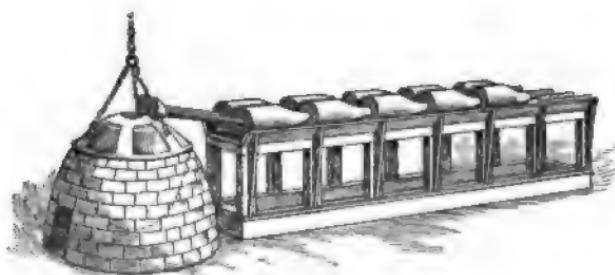


FIG. 46.—Apparatus for purifying iodine.

gently in an iron pot with a lead cover, which is connected with two rows of bottle-shaped condensers (Fig. 46). The iodine, which collects in these condensers, is purified by washing and resubliming. (2) In another process the mother liquor from the Chili saltpeter is mixed with acid sodium sulphite ( $\text{HNaSO}_3$ ), and the precipitated iodine is collected on coarse cloth, washed, dried, and then resublimed, as described above.

Courtois, a French chemist, discovered iodine, in 1812, in an attempt to prepare potassium nitrate from seaweed. Davy and Gay-Lussac established its elementary nature and discovered many of its properties. The present name was given by Davy.

**Properties.**—Iodine is a dark grayish crystalline solid, resembling graphite in luster. It crystallizes in plates which have the specific gravity 4.95. It is volatile at the

ordinary temperature, and when gently heated the vapor which is formed has a beautiful violet color. This color suggested the name *iodine* (from the Greek word *iodes*, violetlike). The vapor is nearly nine times heavier than air, and has an odor resembling dilute chlorine, though less irritating. When the vapor is heated, its color changes from violet to deep blue, and the density decreases. Experiment indicates that at about 700° C. the molecules contain only two atoms, and as the temperature rises the molecules slowly dissociate, until at about 1700° C. the iodine vapor consists entirely of atoms. Iodine stains the skin yellow, and turns cold starch solution blue. The presence of a minute trace of iodine may be thus detected, one part of iodine in over 400,000 parts of water producing the blue color. The exact nature of this blue compound is unknown. The presence of starch in many vegetable substances can be shown by this delicate test. Iodine dissolves slightly in water, and freely in alcohol, chloroform, carbon disulphide, ether, and potassium iodide solution. The chloroform and carbon disulphide solutions are violet, but the others are brown, or even black. The chemical properties of iodine resemble those of chlorine and bromine, but it is less active. Bromine and chlorine displace iodine from its compounds, chlorine and chlorine water being often used for this purpose. It combines directly with other elements and replaces some. Phosphorus bursts into a flame when combining with iodine.

**Compounds of Iodine** resemble the corresponding ones of chlorine and bromine. Hydriodic acid is much like hydrobromic and hydrochloric acid, though unlike them in being a reducing agent. Iodides are salts of hydriodic acid, and like many salts they are prepared in various ways. In general behavior they are similar to bromides and chlorides. **Potassium iodide** ( $KI$ ) is made and used like potassium bromide. Iodates and periodates are known.

**Miscellaneous.** — Iodine dissolved in alcohol or in potassium iodide solution is used as an application for the skin to prevent the spread of eruptions or to reduce swellings. Iodine is used to make medicinal preparations, especially iodoform ( $\text{CHI}_3$ ), which is used as a dressing for wounds. Large quantities of iodine are used in making aniline dyes. Potassium iodide is made in large quantities, Germany alone exporting about 150 tons of it annually. Chili annually exports over 300 tons and Norway over 160 tons of iodine and iodides.

### EXERCISES.

1. What elements constitute the halogen group? Why are they so called?
2. How does fluorine occur in nature? Describe briefly the isolation of fluorine. When was it first performed? Summarize the chief properties of fluorine.
3. How is hydrofluoric acid prepared? Give the equation for the reaction. What are its characteristic properties? For what is it used?
4. How is glass etched? State the essential changes.
5. What is the formula of hydrofluoric acid?
6. How does bromine occur in nature? What are the sources of commercial bromine? What general method is used to prepare this element? Describe briefly the commercial methods. State the chief properties. For what is it used? How does this element differ from all others previously studied?
7. Name several compounds of bromine. What is potassium bromide?
8. Give a brief account of the discovery of (a) bromine and (b) iodine.
9. Discuss the occurrence of iodine in nature. How is iodine prepared (a) in the laboratory and (b) on a large scale? Summarize the properties of iodine. Describe the test for iodine.
10. Name several compounds of iodine. Describe potassium iodide.
11. Compare hydrochloric, hydrobromic, and hydriodic acids.
12. What is the symbol of (a) fluorine, (b) chlorine, (c) bromine, (d) iodine? What is the derivation of the name of each element?
13. Compare the physical properties of fluorine, chlorine, bromine, and iodine.
14. What is "drug-store iodine"?

**PROBLEMS.**

1. What is the percentage composition of (a) fluor spar ( $\text{CaF}_3$ ) and (b) cryolite ( $\text{Na}_3\text{AlF}_6$ )?
2. How much (a) calcium sulphate and (b) hydrofluoric acid are formed by heating 100 gm. of fluor spar with sulphuric acid?
3. Calculate the percentage composition of (a) potassium bromide ( $\text{KBr}$ ), (b) potassium iodide ( $\text{KI}$ ), (c) silver bromide ( $\text{AgBr}$ ), and (d) iodoform ( $\text{CHI}_3$ ).
4. How much potassium iodide is needed to prepare 63.5 gm. of iodine?
5. How much potassium bromide is needed to prepare 10 gm. of bromine?
6. Write the formulas of the following compounds by using the valence tables: Magnesium iodide, mercurous iodide, mercuric bromide, barium fluoride, zinc iodide, ferrous bromide, lead iodide, ferric fluoride, cupric fluoride.
7. Write the equations for the following reactions: (a) Potassium bromide and silver nitrate form silver bromide and potassium nitrate. (b) Sodium iodide and silver nitrate form silver iodide and sodium nitrate.

## CHAPTER XVII.

### SULPHUR AND ITS COMPOUNDS.

**SULPHUR** has been known for ages. The alchemists regarded it as one of the primary forms of matter. The element and its compounds have always played an important part in the development of many industries.

**Occurrence and Formation.**— Sulphur, free and combined, is abundant and widely distributed. Free or native sulphur is found usually in volcanic regions. There are also beds associated with gypsum (calcium sulphate). It is believed that such deposits were formed by the reduction of the gypsum by microorganisms into limestone and sulphur.

Combined sulphur is found in volcanic gases, in substances of vegetable and animal origin, and as sulphides and sulphates. Several important metallic ores are **native sulphides**, e.g. lead sulphide ( $PbS$ ), zinc sulphide ( $ZnS$ ), and those of mercury, antimony, and copper. Probably some native sulphur has been formed by the decomposition of sulphides by heat. The most abundant **sulphates** are varieties of calcium sulphate ( $CaSO_4$ ), barium sulphate ( $BaSO_4$ ), and magnesium sulphate ( $MgSO_4$ ). Volcanic gases often contain sulphur dioxide ( $SO_2$ ) and hydrogen sulphide ( $H_2S$ ). The latter is also found in the water of sulphur springs. Doubtless some of the sulphur found in volcanic districts has been produced from these two gases. Their interaction may be represented thus—



Sulphur is also a component of onions, horse-radish, mustard, garlic, eggs, some petroleum and coal, and certain complex compounds of the body — such as bile and saliva. It has been estimated that the body contains about 125 gm. (0.27 lb.) of combined sulphur.

**Source.** — Sicily, until recently, furnished most of the sulphur, the annual output being about 500,000 tons. Owing to the favorable geographical location, rich deposits, and cheap labor, it was thought the supply would continue to come from there. But enough sulphur for domestic uses is now readily obtained from the vast deposits in Louisiana.

Some of the sulphur of commerce is obtained by roasting iron pyrites, as in the manufacture of sulphuric acid. Small amounts are recovered from the calcium sulphide waste of the Leblanc soda process (see Sodium Carbonate), and from the residues of the iron oxide used to purify illuminating gas.



FIG. 47.—Kiln for extracting sulphur from the crude ore. The calcarone is shown as a vertical section (right) and in operation (left).

**Extraction.** — For many years sulphur has been extracted from the impure native sulphur in Sicily by a primitive process. The crude sulphur is brought to the surface by laborers, piled loosely in a heap, and covered with powdered or burnt ore or with earth. The heap is ignited at the bottom, and the heat produced by the com-

bustion of some of the sulphur melts the rest, which runs out at the bottom (Fig. 47).

In Louisiana the sulphur is obtained in a very pure condition by forcing hot water through pipes down upon the deep beds; the melted sulphur rises part way in another pipe, and is then forced to the surface by compressed air introduced through a small innermost pipe.

**Purification.** — Sulphur obtained from Sicily requires purification. This is accomplished by the apparatus shown in Figure 48. The crude sulphur is melted in *B*, and flows into the iron cylinder, *A*. Here it is heated, and the vapors

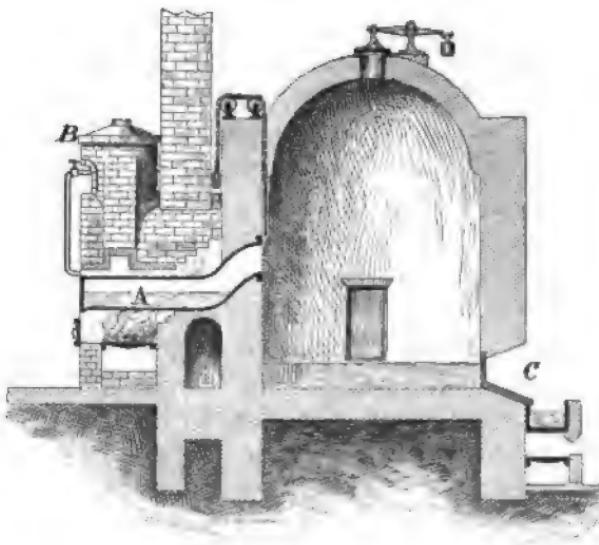


FIG. 48.—Apparatus for purifying sulphur.

pass into the large brick chamber, provided with a tap, *C*, from which the liquid sulphur may be withdrawn. If the distillation is conducted slowly, the sulphur vapor condenses upon the cold walls of the chamber as a fine

powder, called **flowers of sulphur**, just as water vapor suddenly cooled below 0° C. turns to snow. As the operation continues the walls become hot, and the sulphur collects on the floor as a liquid which is drawn off into wooden molds. This is **roll sulphur** or **brimstone**.

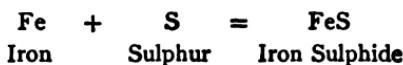
**Properties.**—Ordinary sulphur is a yellow, brittle, crystalline solid. It is insoluble in water, but most varieties dissolve in carbon disulphide, and to some extent in turpentine, chloroform, and benzene ( $C_6H_6$ ). Sulphur does not conduct heat. The warmth of the hand causes it to crackle and even break from the unequal expansion.

The specific gravity of the solid is about 2. The specific gravity of the vapor varies with the temperature. At the lowest temperature at which sulphur can be vaporized, the molecule contains eight atoms ( $S_8$ ), while at 800° C. and higher it contains two atoms ( $S_2$ ).

Heated to 114.5° C. sulphur melts to a thin, amber-colored liquid. As the temperature is raised, the liquid darkens and thickens, until at about 230° C. it is black and too thick to be poured from the vessel. Heated still higher, the color remains black but the mass becomes thin, and finally at about 448° C. the liquid boils and turns into a yellowish brown vapor. Sulphur ignites readily and burns with a pale blue flame, forming sulphur dioxide gas,  $SO_2$ ; if burned in oxygen, a little sulphur trioxide,  $SO_3$ , is also formed. Finely divided sulphur oxidizes in moist air, forming sulphuric acid,  $H_2SO_4$ . It also combines directly and readily with hydrogen, carbon, chlorine, and other elements, especially metals. The compounds formed are **sulphides**.

The reaction between sulphur and metals is often attended by vivid combustion, though heat is necessary to start the chemical action. When a mixture of flowers of sulphur and powdered iron is heated, the mass begins to glow and soon becomes red-hot, the glow often spread-

ing through the mass after removal from the flame. The product is iron sulphide, and the change is represented thus—



Heated copper glows when dropped into melted sulphur, while zinc dust and flowers of sulphur combine with almost explosive violence.

**Different Forms of Sulphur.** — Sulphur exists in at least three different forms,—two crystallized and one amorphous. These modifications differ in specific gravity, solubility, and other properties. The crystallized forms belong to the orthorhombic and monoclinic systems (see Appendix, § 3). According to some authorities these different forms are allotropic modifications of sulphur. **Orthorhombic** sulphur is the form deposited by crystallization from a solution of carbon disulphide (Fig. 49). Crystallized native sulphur is orthorhombic. The monoclinic crystals are deposited from molten sulphur. By melting sulphur in a crucible and pouring off the excess of liquid as soon as crystals shoot out from the walls near the surface, the interior of the crucible when cold will be found to be full of long, dark yellow, shining needles. They are **monoclinic** crystals of sulphur. After a few days they become dull and yellow, and crumble into minute crystals of the orthorhombic form.



FIG. 49.—Orthorhombic sulphur.

**Amorphous** sulphur is formed by pouring boiling sulphur into water. It is a tough, plastic, rubberlike, amber-colored mass, insoluble in carbon disulphide. It is entirely different in color and texture from the crystallized varieties. In a short time it becomes hard, brittle, and yellow, and ultimately acquires many properties of ordinary sulphur.

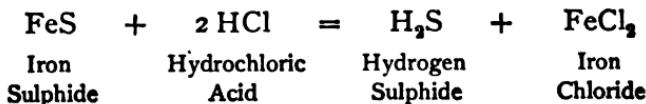
Other varieties of amorphous sulphur are known. They are white or whitish powders. One is made by boiling flowers of sulphur with milk of lime and adding hydrochloric acid to the decanted liquid. A fine sulphur powder is precipitated, which gives the liquid the appearance of milk, hence the name often applied to it, "milk of sulphur."

**Uses.** — Sulphur is used in making sulphuric acid and other sulphur compounds, gunpowder, fireworks, matches, in vulcanizing rubber, as a medicine and a constituent of some ointments, and as a germicide for *Phylloxera* — an insect which destroys grapevines.

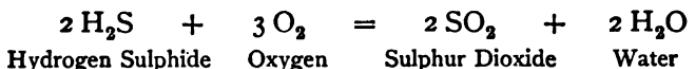
**Compounds of Sulphur.** — The important compounds of sulphur are hydrogen and other sulphides, sulphur dioxide and trioxide, the sulphites, sulphuric acid and the sulphates, and carbon disulphide.

**Hydrogen Sulphide**,  $H_2S$ , is a gaseous compound of sulphur and hydrogen, and is often called **sulphuretted hydrogen**. It occurs in some volcanic gases, and in the waters of sulphur springs. It is often found in the air, especially near sewers and cesspools, since it is one product of the decay of organic substances containing sulphur. It is one of the impurities of illuminating gas, being formed by the union of the sulphur and hydrogen of the coal.

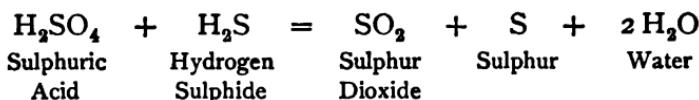
The gas is prepared in the laboratory by the interaction of dilute acids and metallic sulphides, usually hydrochloric acid and ferrous sulphide. When the acid is poured upon fragments of the sulphide, the gas is rapidly evolved without applying heat, and may be collected over water. The equation for the chemical change is —



Hydrogen sulphide gas is colorless and has the odor of rotten eggs. It is poisonous. A little, if breathed, produces headache and nausea, and a large quantity renders one unconscious. This gas is inflammable and burns with a bluish flame, forming water and sulphur dioxide, thus —



If the supply of air is insufficient, combustion is incomplete and sulphur is also formed. It is a powerful reducing agent, and is often used as such in chemical analysis. Even sulphuric acid is reduced by it, thus —

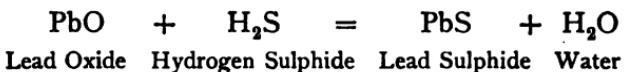


Hydrogen sulphide is soluble in water, one volume of water dissolving about three volumes of the gas at the ordinary temperature. The solution is called **hydrogen sulphide water**, and is often used instead of the gas. The solution reddens litmus and decomposes slowly, sulphur being deposited.

A liter of dry hydrogen sulphide gas, under standard conditions, weighs 1.537 gm. When metals are heated in dry hydrogen sulphide, metallic sulphides are formed and the volume of hydrogen liberated is the same as the original volume of gas. Since the hydrogen molecule is  $\text{H}_2$ , there must be two atoms of hydrogen in the hydrogen sulphide molecule. Its vapor density is 17.15, hence the molecular weight is 34.3. Subtracting 2 for  $\text{H}_2$ , the remainder 32.3 agrees well with the atomic weight of sulphur. Hence, there can be only one atom of sulphur in hydrogen sulphide, and formula must be  $\text{H}_2\text{S}$ .

**Sulphides** may be regarded as salts of the weak acid, hydrogen sulphide, though they are not always prepared directly from hydrogen sulphide. They may be produced

by the direct union of sulphur and metals, as in the case of iron and copper sulphides previously mentioned, or by exposing the metal to the moist gas. A more common way is to precipitate them by passing the gas into solutions of metallic compounds, or, sometimes, by adding hydrogen sulphide water. Copper, tin, lead, and silver are rapidly tarnished by the gas. Silverware, on this account, turns brown or black, especially in houses heated by coal and lighted by coal gas, because hydrogen sulphide is one product of the combustion of coal and gas. The brown silver sulphide also coats silver spoons which are put into mustard or eggs. Lead compounds are blackened by this gas, owing to the formation of lead sulphide, thus —



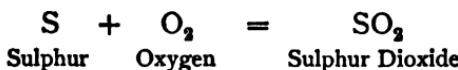
For this reason houses painted with "white lead" paint often become dark, and, similarly, oil paintings are discolored. The blackening of a solution of a lead compound is the customary test for hydrogen sulphide.

Many sulphides have a brilliant color. Arsenious sulphide is pale yellow, cadmium sulphide is golden yellow, manganese sulphide is flesh colored, zinc sulphide is white, antimony sulphide is orange red. They vary in solubility. The sulphides of lead, silver, copper, and some other metals are insoluble in dilute hydrochloric acid. The sulphides of iron, zinc, and some other metals are decomposed by dilute hydrochloric acid, but are precipitated if ammonium hydroxide is present. Sulphides of certain metals dissolve in water. Hence by precipitating metals under different conditions, groups of metals may be separated and subjected to further tests. The color often affords a ready means of detecting each sulphide. Hydrogen sulphide is thus a serviceable reagent in the branch of chemistry called Qualitative Analysis.

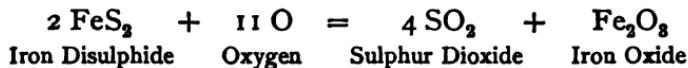
**Sulphur Dioxide,  $\text{SO}_2$ ,** is the common compound of sulphur and oxygen. It occurs in the gases of volcanoes,

and to a slight extent in the atmosphere, since it is the usual product of the combustion of sulphur and sulphur compounds.

When sulphur burns in air (or oxygen), sulphur dioxide is formed, thus —

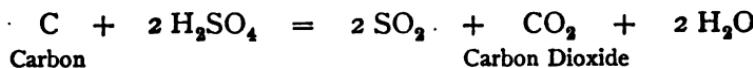
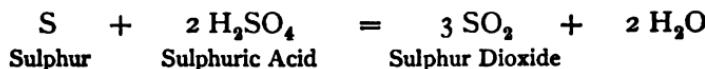


It is also formed by roasting iron disulphide (iron pyrites) in the air, thus —



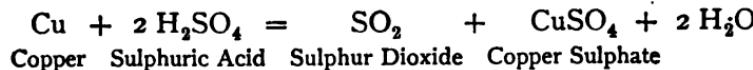
The above reaction is utilized on a large scale in the commercial manufacture of sulphuric acid.

Sulphur and carbon reduce sulphuric acid to sulphur dioxide, thus —

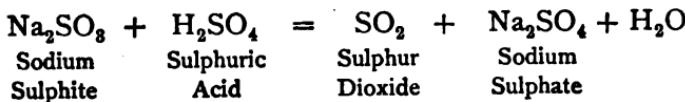


Two methods of preparation are used in the laboratory.

(1) If copper and concentrated sulphuric acid are heated, a series of complex changes results finally in the evolution of sulphur dioxide. The equation is usually written —



(2) Dilute sulphuric (or hydrochloric) acid dropped upon a sulphite yields sulphur dioxide, thus —



This method is convenient for liberating a steady current of the gas.

Sulphur dioxide gas has no color. Its odor is suffocating, being the well-known odor associated with burning sulphur matches. It will not burn in the air, nor will it support ordinary combustion. A burning taper or stick of wood is instantly extinguished by it, but finely divided metals, iron for example, burn in it. It is a heavy gas, the high density (2.2) allowing it to be readily collected by downward displacement. Low temperature and pressure change it into a transparent, colorless liquid, which boils at  $-8^{\circ}\text{ C}$ . and freezes at  $-76^{\circ}\text{ C}$ . into a transparent, icelike solid. It is very soluble in water. At the ordinary temperature one volume of water dissolves about forty volumes of gas, but loses it all by boiling. This solution is sour and reddens blue litmus, and contains sulphurous acid. Moist sulphur dioxide bleaches vegetable coloring matters. A red or a purple flower loses color in it. Silk, hair, straw, wool, and other delicate substances, which would be injured by chlorine, are whitened by sulphur dioxide. In some cases the color returns when the bleached article is exposed to the air for some time, and usually such bleached objects become yellow with age. The coloring matter is not wholly destroyed, but probably unites with the sulphur dioxide to form a colorless compound, which slowly decomposes.

Immense quantities of sulphur dioxide are used in the manufacture of sulphuric acid. The gas is also used to preserve meat and wines, to fumigate clothing and houses, in paper making, in tanning, in refining sugar, and in making acid sodium sulphite. Liquid sulphur dioxide is used in extracting glue and gelatine, and in various metallurgical processes. It absorbs heat during evaporation, and is used in some ice machines.

A liter of sulphur dioxide under standard conditions weighs 2.927 gm.

**The Composition of Sulphur Dioxide** is based on the following : The gas formed by burning sulphur in a measured volume of oxygen has the same volume as the oxygen itself. Hence there are as many molecules of sulphur dioxide as there were of oxygen ; that is, one molecule of sulphur dioxide contains one molecule (or two atoms) of oxygen. A molecule of oxygen weighs 32. But the molecular weight of sulphur dioxide found from its vapor density is about 64. Subtracting 32 (*i.e.*  $2 \times 16$ ) from this, there remains about 32 for sulphur. The atomic weight of sulphur is 32.07, hence sulphur dioxide contains only one atom of sulphur, and its composition is expressed by the formula  $\text{SO}_2$ .

**Sulphurous Acid and Sulphites.** — Sulphurous acid is formed when sulphur dioxide dissolves in water. Sulphur dioxide is, therefore, sulphurous anhydride. The simplest equation expressing this fact is —



The acid has never been obtained free, resembling carbonic acid in this respect. It is unstable, and gradually forms sulphuric acid by combining with oxygen from the air. The acid is dibasic, and forms two classes of salts, the **sulphites**. They are reducing agents, and yield sulphur dioxide when treated with acids. **Acid sodium sulphite** ( $\text{HNaSO}_3$ ), often called bisulphite of soda, is the antichlor used to remove the excess of chlorine from bleached cotton cloth. It is also used in brewing, tanning, and in making starch, sugar, and paper. **Acid calcium sulphite** ( $\text{CaH}_2(\text{SO}_3)_2$ ), prepared by passing sulphur dioxide into milk of lime, is used in paper making.

**Sulphur Trioxide**,  $\text{SO}_3$ , is formed by the direct union of sulphur dioxide and oxygen, a little being produced when sulphur burns in air or in oxygen. The action is slow, but may be hastened by passing a mixture of sulphur dioxide and oxygen (or air) over hot platinum, or over asbestos coated with platinum. Other substances also hasten the change. It is a white, crystalline solid, which melts at  $15^\circ \text{ C}$ . and boils at  $46^\circ \text{ C}$ . Another form, silklike in luster and appearance, is known. When exposed to moist air it

fumes strongly, forming sulphuric acid ; and when dropped into water it dissolves with a hissing sound and evolution of heat, thus —



The vapor density of sulphur trioxide shows that its molecular weight is about 80. Hence the formula ( $\text{SO}_3$ ) harmonizes with the fact that two volumes of sulphur trioxide decompose by heat into two volumes of sulphur dioxide and one volume of oxygen.

**Sulphuric Acid**,  $\text{H}_2\text{SO}_4$ , is found in the waters of a few rivers and mineral springs. It is manufactured in enormous quantities and used for many purposes.

Sulphuric acid was doubtless known to the Arabian alchemists living in the tenth century. It was definitely mentioned by Basil Valentine in the fifteenth century, who describes its preparation by heating a mixture of iron sulphate (green vitriol) and sand. The product, an oily liquid, was called *oil of vitriol*, a name now often used. About 1740, the method of burning sulphur and oxidizing the product was introduced into England.

**The Manufacture of Sulphuric Acid**, as usually conducted, is based upon the fact that the oxidation of sulphur dioxide in the presence of water forms sulphuric acid. The apparent equation for the chemical change is —



The oxidation is accomplished in the older method by oxides of nitrogen and in the newer method by platinum.

The general operation consists in passing sulphur dioxide, air, steam, and oxides of nitrogen into large lead chambers. The oxides of nitrogen in the presence of steam change the sulphur dioxide into sulphuric acid, which collects on the walls and floors of the lead chambers. The oxides of nitrogen which lose part of their oxygen by this

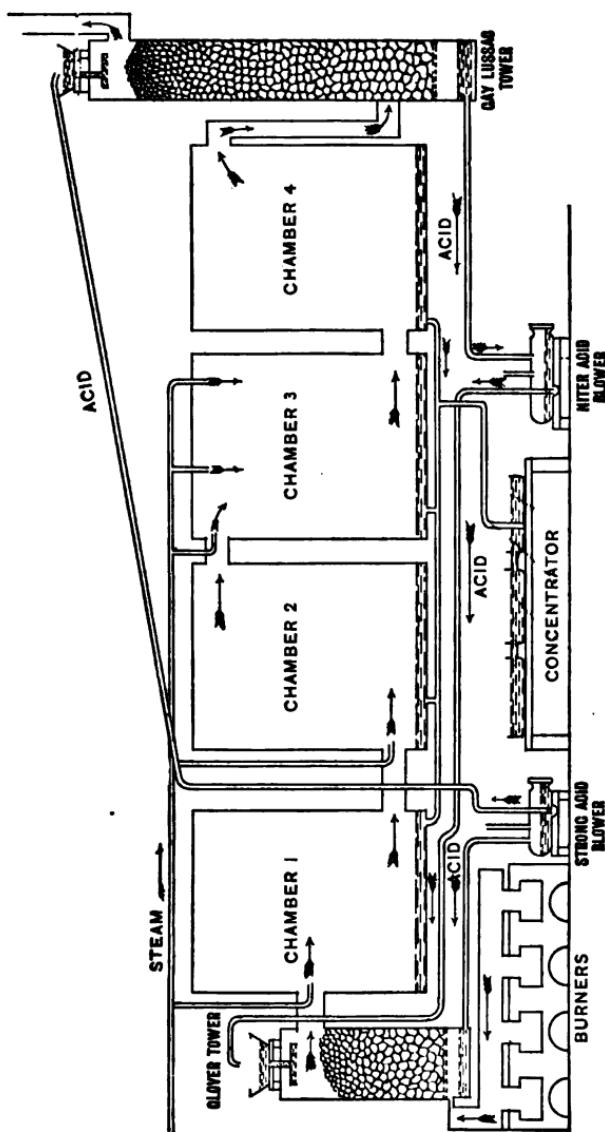
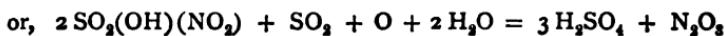
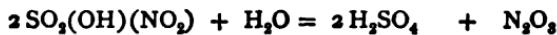
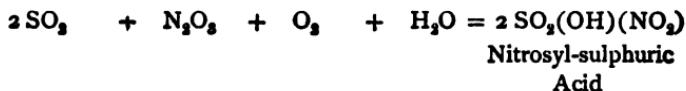


FIG. 50.—Apparatus for manufacturing sulphuric acid by the chamber process.

change are themselves reoxidized by the air into higher oxides. The main parts of a sulphuric acid plant, together with the courses taken by the gases, are shown in Figure 50.

Careful study shows that the chemical changes involved in this process of manufacturing sulphuric acid are complex and variable. According to a reliable authority, the main continuous reactions may be represented thus—

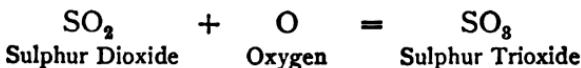


The nitrogen trioxide ( $\text{N}_2\text{O}_3$ ) is the essential factor, though probably the change is really due to a mixture of nitric oxide ( $\text{NO}$ ) and nitrogen peroxide ( $\text{NO}_2$ ). Under some conditions, nitric oxide plays a prominent part. It may be said in general that the ease with which the oxides of nitrogen pass into each other makes it highly probable that they are carriers of oxygen from the air to the sulphur dioxide.

A **Sulphuric Acid Plant** consists of three main parts—(a) the furnace for producing sulphur dioxide, (b) the lead chambers together with the Glover and Gay-Lussac towers for changing the sulphur dioxide into sulphuric acid, and (c) the concentrating apparatus. The manufacture is conducted somewhat as follows: (1) Sulphur or iron disulphide ( $\text{FeS}_2$ ) is burned in a furnace constructed so that enough air passes over the burning mass to change the sulphur into sulphur dioxide, and to furnish the proper amount of oxygen for later changes. In some works the furnace is provided with "niter pots" containing a mixture of sodium nitrate and sulphuric acid; the nitric acid vapors which are formed are one source of the oxides of nitrogen. (2) The mixture of sulphur dioxide, oxides of nitrogen, and air passes from the furnace into the bottom of the **Glover tower**. This is a tall tower filled with small stones over which flow two streams of sulphuric acid, one dilute and the other containing oxides of nitrogen (obtained from the **Gay-Lussac**

tower). These acids not only cool the ascending gases, but are themselves deprived of water and oxides of nitrogen. Hence, concentrated acid flows out of the bottom of the Glover tower, while from the top sulphur dioxide, oxides of nitrogen, steam, and air pass on into the first lead chamber. Here nitric acid is often introduced, as well as steam. The main chemical changes occur in this and in the second chamber. A third chamber serves mainly to cool and dry the gases. These chambers are huge boxes often having a total capacity of 150,000 cubic feet; the walls and floors are of sheet lead supported on a wooden framework, lead being a metal which is only slightly attacked by the chamber acid. The remaining gases pass on into the bottom of the Gay-Lussac tower. This tower is filled with coke over which flows concentrated sulphuric acid (from the Glover tower), which absorbs the unused oxides of nitrogen. These oxides are liberated again in the Glover tower, hence there is little loss. At the end of the plant is a tall chimney, which serves as an exit for unused gases (such as nitrogen) and also creates a draft strong enough to carry the gases through the chambers and tower. (3) The acid which is produced in the chambers and drawn off from them at intervals contains about 67 per cent of the compound  $H_2SO_4$ . Ordinary commercial sulphuric acid which contains about 96 to 98 per cent is prepared from the chamber acid by evaporation, first in lead pans and finally in a platinum or an iron vessel.

Another method of manufacturing sulphuric acid has recently been perfected, called the **contact method**. Sulphur dioxide and air, well purified and heated to 350–400°C., are led through pipes containing plates covered with a contact mixture, which is chiefly finely divided platinum. The sulphur dioxide is oxidized to sulphur trioxide, thus—



The sulphur trioxide is conducted into dilute sulphuric acid or water, thus producing a pure acid of any desired strength. The process is continuous if the gases from the pyrites burners are completely freed from arsenic compounds, sulphur dust, and other impurities.

In the above process the platinum is not changed, nor does it cause the sulphur dioxide to unite with the oxygen. It facilitates the chemical action between the gases somewhat as oil assists the movement of machinery. This kind of chemical action is called **catalysis** or **catalytic action**. The substance which hastens or retards a chemical reaction, but appears unchanged at the end of the process is called a **catalyzer**. In many cases of catalytic action it has been found that the catalyzer probably participates in the chemical action, though its exact share is not always clearly understood.

**Properties of Sulphuric Acid.**—Sulphuric acid is an oily liquid, colorless when pure, but usually brown from the presence of charred organic matter, such as dust and straw. The commercial acid has the specific gravity 1.83. When sulphuric acid is mixed with water, considerable heat is evolved. The acid should always be poured into the water, otherwise the intense heat may crack the vessel or spatter the hot acid. The volume of dilute acid produced is smaller than the sum of the volumes of water and concentrated acid. The tendency to absorb water is shown in many ways. The concentrated acid absorbs moisture from the air and from gases passed through it. It is often used in the laboratory to dry gases, since it is not volatile at the ordinary temperature. Wood, paper, sugar, starch, cotton cloth, and many organic substances are blackened by sulphuric acid. Such compounds contain hydrogen and oxygen in the proportion to form water; these two elements are abstracted and carbon alone remains. Similarly, sulphuric acid withdraws water from the flesh, making painful wounds.

Sulphuric acid is reduced by hydrogen sulphide, hydrobromic and hydriodic acids, carbon, and sulphur; it combines with ammonia to form ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$ ; and is decomposed by all metals except platinum and gold, liberating hydrogen, sulphur dioxide, or hydrogen sulphide.

**Uses of Sulphuric Acid.** — Sulphuric acid is one of the most important substances. Directly or indirectly it is used in hundreds of industries upon which the comfort, prosperity, and progress of mankind depend. It is used in the manufacture of all other mineral acids and many organic acids. It is essential in one process for the manufacture of sodium carbonate, from which in turn are made soap and glass. Enormous quantities are consumed in making artificial fertilizers, alum, nitroglycerine, glucose, phosphorus, dyestuffs, and in various parts of such fundamental industries as dyeing, bleaching, electroplating, refining, and metallurgy.

**Sulphates.** — Sulphuric acid is dibasic and forms two classes of salts, — the **normal sulphates**, such as  $\text{Na}_2\text{SO}_4$ , and the **acid sulphates**, such as  $\text{HNaSO}_4$ . The normal sulphates are stable salts; the acid salts lose water when heated. Most sulphates are soluble in water, only the sulphates of barium, strontium, and lead being insoluble, while calcium sulphate is slightly soluble. Important sulphates are calcium sulphate (gypsum  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ), barium sulphate (heavy spar,  $\text{BaSO}_4$ ), zinc sulphate (white vitriol,  $\text{ZnSO}_4$ ), copper sulphate (blue vitriol or blue stone,  $\text{CuSO}_4$ ), iron sulphate (green vitriol, copperas, ferrous sulphate,  $\text{FeSO}_4$ ), sodium sulphate (Glauber's salt,  $\text{Na}_2\text{SO}_4$ ), and magnesium sulphate (Epsom salts,  $\text{MgSO}_4$ ). Sulphates are widely used in medicine and in many industries.

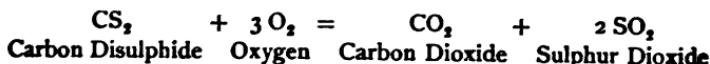
The **test for sulphuric acid or a soluble sulphate** is the formation of the white, insoluble barium sulphate upon the addition of barium chloride solution. An insoluble sulphate fused on charcoal is reduced to a sulphide, which blackens a moist silver coin.

**Fuming Sulphuric Acid**,  $\text{H}_2\text{S}_2\text{O}_7$ , is made by adding sulphur trioxide to sulphuric acid, or by heating moist ferrous sulphate. This is the acid called sulphuric acid by the alchemists. It is sometimes called

**Nordhausen sulphuric acid.** It is a thick, brown liquid, which fumes strongly in the air, owing to the escape of oxides of sulphur. It is used in gas analysis to absorb ethylene and other illuminants, and in dyeing to dissolve indigo. If the fuming acid is cooled to  $0^{\circ}$  C., crystals separate; they are called **pyrosulphuric acid**.

**Sodium Thiosulphate**,  $\text{Na}_2\text{S}_2\text{O}_3$ , is a salt of an unstable acid. It is sometimes incorrectly called sodium hyposulphite, or simply "hypo." It is a white, crystallized solid, very soluble in water. The solution, used in excess, dissolves the halogen compounds of silver; hence its extensive use in photography (see Photography). It also finds some use as an antichlor, and in chemical analysis for determining the amount of free iodine in a solution.

**Carbon Disulphide**,  $\text{CS}_2$ , when pure, is a clear, colorless liquid, with an agreeable odor. The commercial substance is yellow and has an offensive odor. It is poisonous. It is volatile and extremely inflammable, the equation for its combustion being—



This liquid is almost insoluble in water. It dissolves rubber, gums, fats, iodine, camphor, and some forms of sulphur. It is a highly refracting liquid, and hollow glass prisms filled with it are used to decompose light. As a solvent it is used to dissolve pure rubber in the manufacture of rubber cement. It is also used to kill insects on both living and dried plants (*e.g.* in museums), and to exterminate burrowing animals, such as moles and woodchucks. Many oils, waxes, and greases are extracted by carbon disulphide. It is also used to manufacture compounds of sulphur and of carbon.

Until recently carbon disulphide was manufactured by passing sulphur vapor over red-hot coke or charcoal in iron or earthenware retorts; the product required laborious purification. It is now manufactured by an electrothermal process. Several groups of carbon electrodes are set into the base of a furnace, coke is packed loosely around them, and the body of the furnace is filled with charcoal. Sulphur is introduced at suitable points, and when the current passes the sulphur melts, vaporizes, and unites with the heated carbon above the electrodes.

**Selenium** and **Tellurium** are rare elements which form compounds analogous to the principal compounds of sulphur. These three with oxygen form a natural group, their physical properties varying gradually with increasing atomic weight.

**EXERCISES.**

1. What is the symbol and atomic weight of sulphur?
2. Where is free sulphur found? Discuss its formation. In what forms is combined sulphur found? Name five native compounds of sulphur. What animal and vegetable substances contain sulphur?
3. Give a brief account of the sulphur industry in Sicily. How is sulphur purified?
4. What is (*a*) flowers of sulphur, (*b*) brimstone, (*c*) roll sulphur, (*a*) milk of sulphur?
5. Summarize the properties of sulphur, especially its action when heated.
6. Describe the different forms of sulphur.
7. For what is sulphur used?
8. What is hydrogen sulphide? Where is it found? Describe its preparation.
9. Summarize the properties of hydrogen sulphide. State the equation for its combustion. What is its action upon sulphuric acid? What is hydrogen sulphide water?
10. Why is  $H_2S$  the formula of hydrogen sulphide?
11. What are sulphides? How are they formed? Name and describe five. Why does silverware often blacken? What use is made of sulphides in qualitative analysis?
12. What is sulphur dioxide? How is it formed? State one equation for its formation. Describe its preparation. For what is it used?
13. Summarize the properties of sulphur dioxide.
14. Why is  $SO_2$  the formula of sulphur dioxide?
15. What is the volumetric equation for the formation of sulphur dioxide from sulphur and oxygen? How many liters of oxygen are needed to form 5 l. of sulphur dioxide?
16. Discuss sulphurous acid and sulphites.
17. What is sulphur trioxide? How is it prepared? State its chief properties. What is its formula? Why?
18. Give a brief historical account of sulphuric acid. Why is it often called oil of vitriol? What is (*a*) chamber acid, (*b*) Nordhausen acid, (*c*) fuming sulphuric acid, (*d*) pyrosulphuric acid?
19. Upon what fact is the manufacture of sulphuric acid based? In what two general ways is the operation accomplished?
20. Describe the older method of manufacturing sulphuric acid.

21. Describe the contact method of manufacturing sulphuric acid.
22. Define (a) catalysis and (b) catalyst.
23. Summarize the properties of sulphuric acid.
24. Enumerate the important uses of sulphuric acid.
25. Define and illustrate (a) sulphate, (b) normal sulphate, (c) acid sulphate.
26. What is (a) gypsum, (b) white vitriol, (c) green vitriol, (d) blue vitriol, (e) Glauber's salt.
27. Describe the test for (a) sulphuric acid, (b) sulphurous acid, (c) a soluble sulphate, (d) an insoluble sulphate, (e) a sulphite.
28. State (a) the properties, and (b) the uses of sodium thiosulphate. What is its common name?
29. State (a) the properties, and (b) the uses of carbon disulphide. How is it manufactured?

### PROBLEMS

1. Calculate the percentage composition of (a) barium sulphate ( $\text{BaSO}_4$ ), (b) zinc sulphate ( $\text{ZnSO}_4$ ), (c) sodium sulphate ( $\text{Na}_2\text{SO}_4$ ).
2. Calculate the percentage composition of (a) galena ( $\text{PbS}$ ), (b) zinc blende ( $\text{ZnS}$ ), (c) iron pyrites ( $\text{FeS}_2$ ), (d) ferrous sulphide ( $\text{FeS}$ ).
3. What weight and what volume of hydrogen can be obtained from 102 gm. of hydrogen sulphide?
4. What is the weight of a stick of brimstone 10 cm. long and 4 cm. in diameter?
5. How many grams of ferrous sulphide are needed to prepare a liter of hydrogen sulphide gas?
6. Sulphuric acid is 1.8 times heavier than water. How many grams of acid will a liter flask hold?
7. Calculate the weight of oxygen necessary to burn (to sulphur dioxide) 731 gm. of sulphur containing 15 per cent of impurities.
8. A lump of sulphur weighing 32 gm. is burned in air. Calculate (a) the weight of oxygen required, and (b) the weight of sulphur dioxide formed.
9. How many liters of oxygen are needed (a) to form 10 l. of sulphur dioxide by burning sulphur in air, and (b) to change 10 l. of sulphur dioxide to sulphur trioxide?

## CHAPTER XVIII.

### SILICON AND BORON.

**Occurrence of Silicon.** — Silicon does not occur free in nature, being found almost exclusively as silicon dioxide ( $\text{SiO}_2$ ) or as silicates. These compounds are so abundant and widely distributed that approximately one fourth of the earth's crust is silicon. Sand and the different varieties of quartz are silicon dioxide. Most rocks are silicates.

Silicon is not a rare element. It is obtained by heating a special mixture of silicon dioxide and carbon in an electric furnace, or by heating silicon chloride with sodium.

Like carbon, silicon has three allotropic forms, — a brown amorphous powder, a dark grayish mass like graphite, and steel-colored crystals. Amorphous silicon may be changed into the other forms. They have different properties.

The name "silicon" comes from the Latin word *silex*, flint.

**Silicon Dioxide or Silica**,  $\text{SiO}_2$ , is the most common compound of silicon. Sand, gravel, sandstone, and quartzite are almost wholly silica. It is an essential ingredient of many rocks, as granite and gneiss. Quartz is silicon dioxide. It has many varieties, which differ in color and structure, due to minute impurities or to the mode of formation. Among the crystalline varieties are the clear, colorless **rock crystal**, the purple **amethyst**, and the rose, yellow, glassy, milky, and smoky forms. Varieties imperfectly crystalline or amorphous are the waxlike **chalcedony**, the various forms of agate having different colored layers, the reddish brown **carnelian**, the black and white **onyx**, the

red or brown **jasper**, the dull brown or black **flint**, and the brittle **chert**. **Opal** is hydrated silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ). **Petrified** or **silicified wood** is largely some variety of quartz which has replaced the woody fiber. There is a "petrified forest" in Arizona. Infusorial or diatomaceous earth is a variety of silica consisting of the shells of minute organisms called *diatoms* (Fig. 51). Quartz is often found as crystals which consist usually of a six-sided prism with a six-sided pyramid at one or both ends, but the crystals are sometimes complex (Fig. 52).

Quartz crystals and



FIG. 51.—Earth from Richmond, Va., containing diatoms.

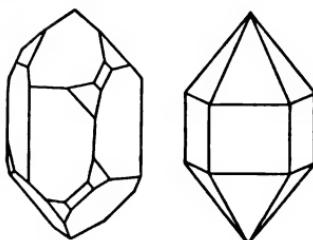


FIG. 52.—Quartz crystals.

varieties like them are hard enough to scratch glass. They are insoluble in water and acids, except hydrofluoric acid, but are soluble in melted hydroxides and carbonates of sodium and potassium. Quartz is infusible, except at very high temperatures. If fused with certain precautions, the molten mass can be drawn out into elastic threads and also shaped into tubes, crucibles, etc., which do not crack by sudden heating and cooling.

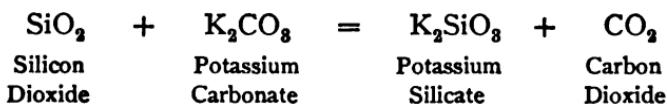
Sandstone and quartzite are used as building stones, and hard sandstone is made into grindstones and whetstones. Sand is used in making sandpaper, glass, porcelain, and

mortar. Glass is roughened and cut by blowing or "blast-ing" fine sand against it. Many of the varieties of quartz are cut and polished into ornaments and gems, *e.g.* amethyst, opal, and agate. Rock crystal is used as the "diamond" in cheap jewelry, and is cut into lenses for eyeglasses and optical instruments. Petrified wood is cut and polished into table tops, mantelpieces, and fireplaces. Infusorial earth is used to polish silver, "electro-silicon" being the commercial name of one kind, and in making cement, "soluble glass," dynamite, and refractory brick. Over 1300 tons are annually used in the United States.

**Silica and Plants.**—Ashes of many plants contain silica, showing that some compound of silicon is assimilated by the plant from the soil — probably silicic acid or a soluble silicate (see below). The ashes of rye and wheat straws and of potato stems contain from 40 to 70 per cent of silica. Plants like horsetail, sword grass, and bamboo are rich in silica. The silica is probably not a plant food in the strict sense, but gives firmness to the tall stalks, especially to their joints, and produces the tough exterior coating, as on the bamboo. The quills of feathers and the spikes of sponges are tough and rigid from the silica they contain.

**Silicon Tetrafluoride ( $\text{SiF}_4$ )** is formed by the interaction of silicon dioxide and hydrofluoric acid, as described under etching (see Etching).

**Silicic Acid and Silicates.**—When silicon dioxide is fused with sodium or potassium carbonates, the corresponding silicate is formed thus —



Potassium and sodium silicates dissolve in water, and when hydrochloric acid is added, the gelatinous precipitate formed is a silicic acid having the formula  $\text{H}_2\text{SiO}_3$  (prob-

bly). This acid is decomposed, by heating, into silicon dioxide and water, thus —



There are many complex silicic acids. **Silicates** are salts of silicic acids, though they are often so complex that no actual corresponding acid is known. Silicates make up a large part of the earth's crust, silicates of aluminium, iron, calcium, potassium, sodium, and magnesium being the most abundant. Many common rocks and minerals are silicates, *e.g.* feldspar, mica, mica schist, hornblende, clay, slate, beryl, garnet, serpentine, and talc.

Sodium and potassium silicates are the only ones soluble in water, and the thick, sirupy solution is often called "water glass" or soluble silica. It is used in making yellow soaps, cements, and artificial stone, to fix colors in frescoing and calico printing, and to render cloth, wood, and paper fireproof.

Some forms of silica dissolve in a hot solution of sodium carbonate. Hence, many hot springs, as in the Yellowstone Park, contain silica in solution (as an alkaline silicate), and when the water comes to the surface and cools, silica is deposited around the spring in beautiful forms called **geyserite** or **siliceous sinter**. Probably the formation of petrified wood is due to the deposition of silica from such a solution.

**Silicides** are compounds of silicon and other elements. Carborundum, carbon silicide (or silicon carbide, CSi), has been mentioned (see Carborundum, Chapter X). Silicides of iron, chromium, and copper ( $\text{Fe}_2\text{Si}$ ,  $\text{Cr}_2\text{Si}$ , and  $\text{Cu}_2\text{Si}$ ) are also commercially important.

**Glass** is a mixture of silicates, one of which is always a silicate of potassium or sodium. Window glass is a silicate of sodium and calcium, and Bohemian glass is a silicate of potassium and calcium. In flint glass, calcium is replaced by lead.

Glass is not made by mixing silicates, but by melting together sand, an alkali, and a calcium or a lead compound. The alkali may be sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), or potassium carbonate ( $\text{K}_2\text{CO}_3$ ), or a mixture of these; sodium sulphate is often used. The calcium compound used is calcium carbonate ( $\text{CaCO}_3$ ) in the form of chalk or limestone. The lead compound used is litharge ( $\text{PbO}$ ) or red lead ( $\text{Pb}_3\text{O}_4$ ). Small quantities of other substances are also used, *e.g.* broken glass to help lower the melting point of the mixture, oxide of arsenic ( $\text{As}_2\text{O}_3$ ), potassium nitrate ( $\text{KNO}_3$ ), or manganese dioxide ( $\text{MnO}_2$ ) to remove the greenish color caused by iron compounds, metallic oxides or other substances to produce colored glass, and numerous ingredients, such as calcium fluoride or calcium phosphate, to make special kinds of glass.

The process consists in heating the proper mixture in a fire-clay pot to a high temperature. During the melting, gases escape, and the impurities, which rise to the surface as a scum, are removed. The molten mass is allowed to cool until it becomes pasty. In this condition it may be blown, welded, cut, drawn, or molded into almost any desired shape.

The mixture used varies with the kind of glass to be made. A typical mixture for table and bottle glass, used in a large works, is —

Sand . . . . .	1550 lb.
Sodium carbonate . . . . .	550 lb.
Lime . . . . .	200 lb.
Sodium nitrate . . . . .	100 lb.
Total charge . . . . .	2400 lb.

**Window Glass** is made by blowing a lump of glass into a hollow globe and then into a cylinder; this on being opened at both ends and cut lengthwise spreads open flat. **Plate glass**, which has about the

same composition as window glass, is made by pouring the molten glass upon a large table, rolling it with a hot iron roller, and subsequently grinding and polishing it. Plate glass is used for large windows and for mirrors, but considerable rough plate is used for skylights and floors. Crown glass is a good quality of window glass. It has a brilliant surface. Limited quantities are used as "bull's eyes" in decorative windows. Bohemian glass is the hard glass of which much chemical apparatus is made. Flint glass is a silicate of potassium and lead; it is a lustrous, soft glass, largely used in making lamp chimneys and globes. Pure flint glass is often called strass or paste, and on account of its luster and brilliancy it is made into artificial gems. Lenses for telescopes and other optical instruments usually consist of both crown and flint glass. Cut glass is flint glass. The object is first molded or blown into the general shape, the design is then cut into the soft glass by a wheel, and the finished object is polished by a wooden wheel smeared with rouge (oxide of iron) or putty.

Many objects, such as tumblers and small dishes, are now made by pressing the soft glass with a die or by blowing it into a mold. Fruit jars, bottles, and lamp chimneys are blown by machinery. Many other improvements have increased the output and improved the quality of glass.

All glassware must be cooled slowly to prevent the glass from being brittle. This operation is called annealing, and is accomplished by passing the objects slowly through a furnace in which the temperature is gradually lowered.

Glass is colored by adding different substances which dissolve in the molten mass. Iron and chromium compounds make it green, the green color of many bottles and fruit jars being due to the iron in the cheap materials used; copper and cobalt compounds produce different shades of blue; manganese dioxide gives a pink or a violet, and a mixture of manganese dioxide and iron oxide gives an orange color; yellow is produced by charcoal, sulphur, or silver; certain copper compounds or gold give a ruby color; translucent or white glass is made by adding fluor spar or cryolite; smoked glass contains nickel; iridescent glass is made by exposing it to the vapors of hydrochloric acid or of tin chloride ( $\text{SnCl}_4$ ).

The United States produces yearly over 50,000,000 dollars' worth of glass. The industry is carried on in about twenty-five states, Pennsylvania producing two fifths of the total output.

**BORON.**

**Occurrence.**— Boron is never found free, but the compounds, borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ), are abundant.

Boron itself is an uncommon element. It is prepared by heating the oxide ( $\text{B}_2\text{O}_3$ ) with magnesium, aluminium, sodium, or potassium. It is greenish brown amorphous powder, without taste or odor. It burns when heated in air, forming the oxide ( $\text{B}_2\text{O}_3$ ). It also unites with the halogens, sulphur, and nitrogen. It forms many borides, one of which, carbon boride ( $\text{CB}_4$ ), is said to be harder than diamond.

**Boric Acid**,  $\text{H}_3\text{BO}_3$ , is contained in the waters and steam of certain volcanic regions, notably Tuscany. Large basins or tanks are built around these steam jets, and are arranged so that the water flows at intervals from one reservoir into the next lower, constantly becoming charged with more boric acid, as the steam condenses. The final solution is evaporated by aid of the heat from the steam jets, and the crude boric acid which settles out is purified by recrystallization. This compound is sometimes called **boracic acid**.

Considerable boric acid is also made in California from borax, and in Germany from the boracite found at Stassfurt.

Boric acid crystallizes in lustrous, white flakes, which feel greasy. It dissolves slightly in cold water, readily in hot water, and in alcohol. When the alcoholic solution is burned, a boron compound colors the vapor green. This is the **test for boron compounds**.

Boric acid is used in making borax, in the manufacture of enamels and glazes for pottery, as an antiseptic in medicine and surgery, and for preserving meat, fish, milk, butter, beer, and wine.

**Borax**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ , occurs in large quantities in California, and an impure borax called tinkel comes from Tibet. Much of the commercial borax is made from

boric acid or from native calcium borate (colemanite,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O}$ ) by boiling with sodium carbonate and separating the borax by crystallization.

Borax is a white crystallized solid, having ten or five molecules of water of crystallization. It effloresces in the air. When heated, ordinary borax melts, then swells up into a white porous mass, which finally becomes a glassy solid. This glassy borax dissolves metallic substances, especially oxides. If the borax is melted on the end of a looped platinum wire, the transparent globule is called a **borax bead**. These beads differ in color under different circumstances, and the oxides of metals cause the beads to assume colors which are characteristic of the metals, as may be seen by the following table:—

#### COLORS OF BORAX BEADS.

METAL.	OXIDIZING FLAME.		REDUCING FLAME.	
	Hot.	Cold.	Hot.	Cold.
Chromium . .	Reddish yellow	Yellowish green	Green	Green
Cobalt . . .	Blue	Blue	Blue	Blue
Copper . . .	Green	Greenish Blue	Colorless	Red
Manganese . .	Violet	Violet	Colorless	Colorless

The bead test is often used in chemistry to confirm other observations or to suggest further examination.

Borax is used in the manufacture of enamels and glazes, and in the formation of the "paste" for artificial gems. Considerable borax is used for preserving canned meat and fish. It is a cleansing agent, and large quantities are consumed in laundries as well as in the manufacture of

soaps, particularly those intended for use in hard water (see Soap). Its power to dissolve oxides adapts it for use in soldering metals. Solder adheres only to clean metals, so a little borax is used to dissolve the film of oxide on the surfaces to be joined. It is likewise used in welding metals and as a flux in their preparation. Considerable quantities are used as a mordant in calico printing and in dyeing. It is an ingredient of ointments, lotions, and powders, which are designed to relieve hoarseness or skin eruption.

#### EXERCISES.

1. What is the symbol and atomic weight of (*a*) silicon, and (*b*) boron?
2. How is silicon found in nature? What proportion of the earth's crust is combined silicon?
3. Name several common forms of silicon dioxide. Describe the different varieties of quartz.
4. What is (*a*) petrified wood, (*b*) opal, (*c*) diatomaceous earth, (*d*) "electro-silicon"?
5. Summarize the properties of quartz. How can it be readily distinguished from other minerals and rocks?
6. State the uses of the different forms of silicon dioxide.
7. Discuss the relation of silicon dioxide to plants.
8. Review with special reference to silicon compounds (*a*) carbborundum, and (*b*) etching glass.
9. Describe the formation and state the properties of ordinary silicic acid. Name several common silicates. What metals are components of silicates?
10. Describe the formation, state the uses, and enumerate the properties of "water glass."
11. What is glass? How is it made? Name the components of the different kinds.
12. What is (*a*) window glass, (*b*) plate glass, (*c*) Bohemian glass, (*d*) flint glass, and (*e*) cut glass?
13. How is glass (*a*) annealed, and (*b*) colored?
14. How is boron found in nature? What is the formula of (*a*) borax, and (*b*) boric acid?

15. Where is boric acid found? How is it manufactured? State its properties and uses.
16. Where is borax found? How is it prepared for commerce? State its properties and uses.
17. Describe the borax bead. State and illustrate its use.

#### PROBLEMS.

1. Calculate the percentage composition, of (a) willemite ( $Zn_2SiO_4$ ), (b) steatite ( $Mg_3Si_4O_{11} \cdot H_2O$ ), (c) quartz ( $SiO_2$ ).
2. What per cent of borax ( $Na_2B_4O_7 \cdot 10 H_2O$ ) is boron?

## CHAPTER XIX.

### PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH.

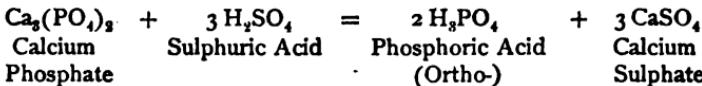
PHOSPHORUS, arsenic, antimony, and bismuth, together with nitrogen, form a natural group of elements.

#### PHOSPHORUS.

**Occurrence.** — Free phosphorus is not found in nature, but phosphates are numerous and abundant. The most common are phosphorite (impure  $\text{Ca}_3(\text{PO}_4)_2$ ) and apatite ( $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$  or  $\text{CaF}_2$ ). About 0.1 per cent of the earth's crust is phosphorus. Calcium phosphate is present in all fertile soils, being a product of decayed rocks. Phosphorus compounds are essential constituents of plants and of the brain, nerves, and bones of animals.

Phosphorus was discovered in 1669 by Brand, who obtained it by heating a certain kind of animal matter. Scheele, in 1771, extracted it from bones.

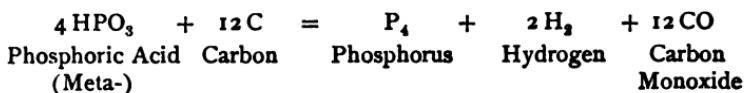
**Preparation.** — Phosphorus is too dangerous a substance to prepare in the laboratory. (1) It is manufactured from bone ash or from native phosphates. The finely ground material is mixed in large vats with enough sulphuric acid to produce the following change:—



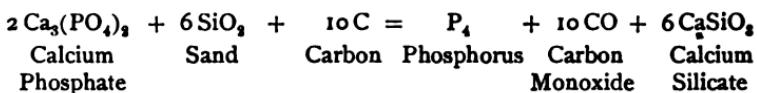
The insoluble calcium sulphate is removed by filtering the mixture through cinders. The phosphoric acid solution is concentrated, mixed with sawdust, coke, or charcoal, and dried, being changed thereby according to the equation—



The dried mass is heated to a high temperature in clay retorts arranged in tiers (Fig. 53), the change thus produced being substantially—



The phosphorus distils as a vapor through a pipe into a trough of water, where it collects as a heavy liquid. (2) Phosphorus is also manufactured in the electric furnace. A mixture of a phosphate, carbon, and sand is fed into a furnace provided with an outlet pipe through which the phosphorus vapor passes into a condenser. The residue is drawn off as a slag at the bottom. The equation for the chemical change is —



Either method gives a black product, which is purified by redistillation in an iron retort, or by oxidation under water with sulphuric

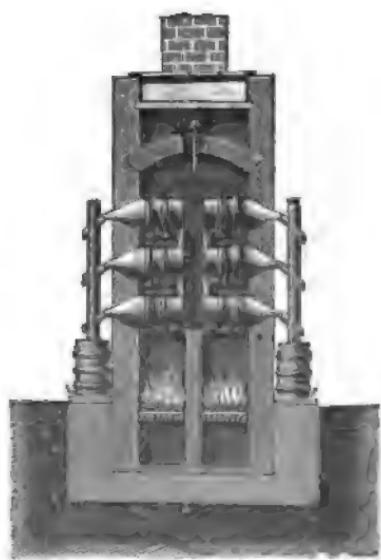


FIG. 53. — Apparatus for the manufacture  
of phosphorus.

**Properties.**—Phosphorus has three allotropic modifications,—yellow or ordinary, red or amorphous, and black or crystalline. **Ordinary phosphorus** is a yellowish, translucent solid. The color deepens by exposure to light. At ordinary temperatures phosphorus is like wax, but at low temperatures it is brittle. Under water it melts at  $44^{\circ}\text{C}$ . Exposed to the air it immediately

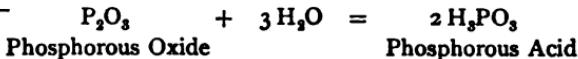
gives off white fumes, and at 34° C. takes fire and burns with a brilliant flame, the main product being phosphorus pentoxide ( $P_2O_5$ ). In moist air it glows, as may be easily seen by rubbing the head of a match in a dark room. This property gave the element its name (from the Greek word *phosphorus*, light bringer). The ease with which it ignites makes phosphorus dangerous to handle. Burns from it are severe and hard to heal. It is very poisonous, and the workmen in phosphorus factories are subject to a dreadful disease, which rots the bones. A fatal dose is about 0.15 gm. Phosphorus is kept beneath water, and should never be handled or cut unless so covered. It is nearly insoluble in water, but dissolves in carbon disulphide and slightly in sodium hydroxide solution. Yellow phosphorus has a faint odor, which may be easily detected by smelling a match head. **Red phosphorus** is made by heating ordinary phosphorus to 250°–300° C. in a closed vessel. Any unchanged yellow phosphorus is extracted with sodium hydroxide solution. The red phosphorus is usually a reddish brown powder, though sometimes it is a brittle mass. It is opaque and odorless, does not give light, nor can it be easily ignited. It is not poisonous, and does not dissolve in carbon disulphide. Its specific gravity is 2.25, that of the yellow form being 1.836. It can be handled without danger. Heated to about 260° C. in an atmosphere of nitrogen or carbon dioxide, it changes into ordinary phosphorus.

**Black Phosphorus** is formed by dissolving red phosphorus in melted lead, and allowing crystals to separate. Its specific gravity is 2.34.

The **vapor density of phosphorus** is such that its molecule must contain four atoms, hence its molecular formula is  $P_4$ .

Certain rat and bug poisons contain ordinary phosphorus, but most of the phosphorus of commerce is consumed in the manufacture of matches (see below).

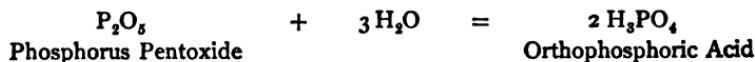
**Oxides of Phosphorus.** — The two important oxides are phosphorous or trioxide ( $P_2O_3$  or  $P_4O_6$ ) and phosphoric or pentoxide ( $P_2O_5$ ). **Phosphorous oxide** is a white solid formed by the slow oxidation of phosphorus or by burning phosphorus in a limited supply of air. It has the odor of phosphorus and is poisonous. Warmed in the air, it changes into the pentoxide. It unites with water to form phosphorous acid, thus —



**Phosphoric Oxide** ( $P_2O_5$ ) is the white, snowlike solid formed by burning phosphorus in an abundant supply of air. It is very deliquescent, quickly withdrawing moisture from the air and combining vigorously with water with a hissing noise. It resembles sulphur trioxide in its power to char wood and paper by withdrawing from them the elements of water. It is often used in the laboratory to dry gases.

**Acids and Salts of Phosphorus.** — There are three phosphoric acids, — orthophosphoric ( $H_3PO_4$ ), metaphosphoric ( $HPO_3$ ), and pyrophosphoric ( $H_4P_2O_7$ ). Phosphorous acid ( $H_3PO_3$ ) and hypophosphorous acid ( $H_3PO_2$ ) are important compounds.

**Orthophosphoric Acid** is a by-product in the manufacture of phosphorus from bone ash (see above); it may be made by oxidizing red phosphorus with nitric acid, or by dissolving phosphorus pentoxide in hot water, thus —



It is a white, crystalline deliquescent solid.

**Metaphosphoric Acid** is formed by heating orthophosphoric acid to a high temperature, thus —



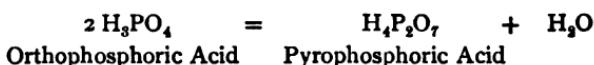
It may be formed by dissolving the pentoxide in cold water, thus —



At ordinary temperature it is a glassy solid, and is called **glacial phosphoric acid**. It dissolves readily in water, and the solution changes into orthophosphoric acid — slowly in the cold, rapidly when boiled.

## Phosphorus, Arsenic, Antimony, Bismuth. 269

**Pyrophosphoric Acid** is formed by heating orthophosphoric acid to  $200^{\circ} - 300^{\circ}$  C., thus —

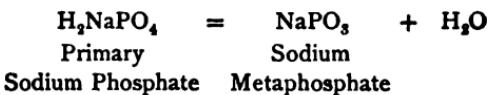


A sodium salt of the ortho-acid is usually used. It may also be formed thus —

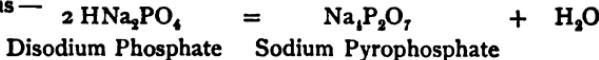


This acid is an amorphous, glassy (but sometimes crystalline) solid. It is readily soluble in water, and its solution behaves like metaphosphoric acid.

Orthophosphoric acid is tribasic, and its salts, the **phosphates**, are numerous. The most important is the normal calcium salt,  $\text{Ca}_3(\text{PO}_4)_2$ . Hydrogen disodium phosphate ( $\text{HNa}_2\text{PO}_4$ ) is the commercial sodium phosphate. This salt and hydrogen sodium ammonium phosphate, or **microcosmic salt** ( $\text{HNa}(\text{NH}_4)\text{PO}_4$ ), are used in chemical analysis. The "acid phosphate" sold as a beverage is a solution of one or more acid calcium phosphates ( $\text{HCaPO}_4$  and  $\text{H}_4\text{Ca}(\text{PO}_4)_2$ ). **Metaphosphates** are formed by heating primary (or mono-) sodium phosphates, thus —

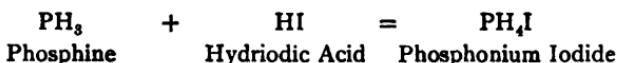


**Pyrophosphates** are formed by heating secondary (or di-) phosphates, thus —



**Hypophosphites** are produced by treating phosphorus with alkalies. They are often used as medicines.

**Other Compounds of Phosphorus.** — **Phosphine** ( $\text{PH}_3$ ) is analogous to ammonia ( $\text{NH}_3$ ), though it is not alkaline. It is made by heating sodium (or potassium) hydroxide with phosphorus. It is poisonous, has a disagreeable odor, and burns in the air, owing to the presence of an inflammable compound of phosphorus and hydrogen. Phosphine itself does not burn. It combines with other substances, forming **phosphonium compounds**, which are analogous to ammonium compounds, e.g. —



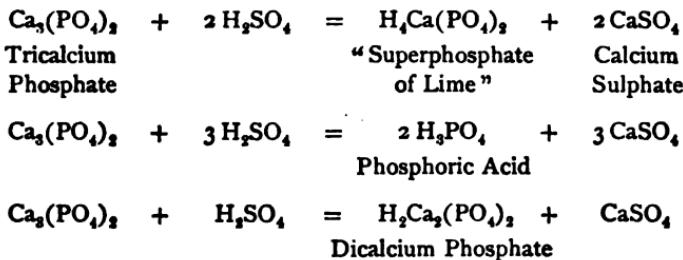
**Phosphorus Trichloride** ( $\text{PCl}_3$ ) is a disagreeable smelling liquid, made by the combustion of dry chlorine and phosphorus; and **phosphorus pentachloride** ( $\text{PCl}_5$ ) is a greenish solid made by passing chlorine into a vessel containing the trichloride.

**Matches.**—Phosphorus is chiefly used in the manufacture of matches. Soft wood is cut by machinery into the desired shape. The cards or sticks are fixed in a frame, and one end is first dipped into melted sulphur or paraffin and then into the phosphorus mixture. The latter consists usually of different proportions of phosphorus, manganese dioxide, glue, and a little coloring matter. Manganese dioxide may be replaced by other oxidizing agents. These matches are the ordinary friction or sulphur kind. By rubbing them on a rough surface enough heat is generated to cause the phosphorus to unite with the oxygen of the oxidizing agent, and the heat thereby produced sets fire to the sulphur or paraffin, and this in turn kindles the wood. Since these matches are poisonous, and liable to take fire, their manufacture has been prohibited in some countries (*e.g.* Switzerland and the Netherlands). Safety matches, which replace them, contain no yellow phosphorus. The head of this kind is usually a colored mixture of antimony sulphide, potassium chlorate, and glue; while the surface upon which the match must be rubbed to light is coated with a mixture of red phosphorus, glue, and powdered glass. Matches are made by machinery, several million being produced in one day.

**Relation of Phosphorus to Life.**—Phosphorus is essential to the growth of plants and animals. Plants take phosphates from the soil and store up the phosphorus compounds, especially in their fruits and seeds. Animals eat this vegetable matter, assimilate the phosphorus compounds, and deposit them in the bones, brain, and nerve

tissue. Bones contain about 60 per cent of calcium phosphate. Part of the combined phosphorus consumed by animals is rejected by them, and often finds its way back into the soil.

The constant removal of phosphates by plants would soon exhaust the soil. Hence phosphorus is restored to the soil in the form of natural or artificial fertilizers. Natural fertilizers are (1) **stable refuse**, which always contains some of the phosphates from the food originally fed to the animals; (2) **guano**, which is the dried excrement and carcasses of the sea birds that once lived in vast numbers in Peru and Chili; and (3) **phosphate slag**, which is a phosphorus by-product obtained in manufacturing steel. These and bones are ground and spread upon the soil. Artificial fertilizers are made from **phosphate rock**. This occurs in large beds in South Carolina, Tennessee, and Florida, which yield about a million tons a year. It consists of the hardened remains of land and marine animals, and is mainly tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ). It is insoluble in water, and must be changed into the soluble monocalcium salt ( $\text{H}_4\text{Ca}(\text{PO}_4)_2$ ), so that it can be evenly distributed through the soil and easily taken up by plants. This soluble salt is called "superphosphate of lime." When phosphate rock is treated with sulphuric acid, the changes involved may be written thus —



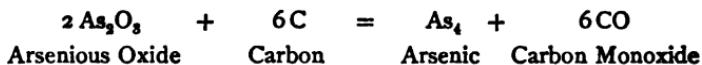
The aim is to convert the crude phosphate rock into "superphosphate," but the three reactions usually occur. The product is ground, dried, and packed in bags for the market. On standing, it may undergo "reversion," i.e. the "superphosphate" and phosphoric acid may form insoluble phosphates, thus making the fertilizer less valuable. Sometimes "superphosphate" is mixed with compounds of nitrogen and of potassium to form a **complete fertilizer**.

## ARSENIC.

**Occurrence.**—Arsenic is found free in nature, but it usually occurs combined with sulphur or a metal, or with both. The common arsenic ores are realgar ( $\text{As}_2\text{S}_3$ ), orpiment ( $\text{As}_2\text{S}_3$ ), arsenic pyrites or mispickel ( $\text{FeSAs}$ ). Arsenic trioxide or arsenolite ( $\text{As}_2\text{O}_3$ ) is also found. Small quantities of arsenic occur in many ores.

The United States annually imports over 6,000,000 pounds of arsenic and its compounds, mainly from England and Germany.

**Arsenic is prepared** in the laboratory by heating a mixture of arsenious oxide and charcoal in a glass tube. The change is represented thus—



On a large scale it is extracted from its ores either by the above method or by roasting arsenic pyrites ( $\text{FeSAs}$ ) in the absence of oxygen.

Arsenic has marked **properties**. It is a brittle, steel-gray solid. A freshly broken piece has a metallic luster, which disappears slowly in a moist atmosphere. It tends to crystallize. The specific gravity is from 5.62 to 5.96. Heated in the air, it volatilizes without melting, and the vapor has an odor like garlic. At about  $180^\circ\text{C}$ . it burns in the air with a bluish flame, forming the white oxide ( $\text{As}_2\text{O}_3$ ). The molecules of arsenic vapor at about  $650^\circ\text{C}$ . contain four atoms. In some respects arsenic resembles both metals and non-metals. It is used to harden the lead which is made into shot.

**Arsenious Oxide or Arsenic Trioxide**,  $\text{As}_2\text{O}_3$ , is the most important compound of arsenic, and is often called simply "arsenic" or "white arsenic." It is found free in nature, but is usually manufactured by roasting arsenic ores. There are two common varieties, a white, granular powder and an amorphous, glasslike solid. It has no odor, a faint, metallic taste, dissolves slightly in cold water, but readily in hot hydrochloric acid. *Arsenic trioxide is a*

*rank poison.* The antidote is fresh ferric hydroxide, which is made by adding ammonium hydroxide to a ferric salt, e.g. ferric chloride. Small doses (2 to 3 grains) are usually fatal, but by habitual use the system appropriates larger doses without ill effects. Workmen in arsenic factories often accidentally swallow with impunity quantities which would ordinarily prove fatal. It is used for making pigments for green paints, for fly and rat poison, in making glass, arsenic compounds, in calico printing, and in preserving skins. As a medicine it is used to purify the blood.

**Other Arsenic Compounds.** — The native mineral **orpiment** ( $As_2S_3$ ) is used in making a yellow paint, and **realgar** ( $As_2S_2$ ) a red paint. **Scheele's green** is chiefly copper arsenite ( $HCuAsO_3$ ), and was formerly used to make a cheap green paint and to color wall paper. The complex arsenic compound **Paris green** is a light green powder; owing to its poisonous character it is used to exterminate potato bugs and other insects. Arsenic forms acids analogous to the acids of phosphorus, though they are less important. The salts **sodium arsenate** ( $HNa_2AsO_4$ ) and **arsenite** ( $NaAsO_2$ ) are used in dyeing. The formation of the yellow sulphide ( $As_2S_3$ ) by passing hydrogen sulphide into an arsenic solution containing hydrochloric acid is the usual **test for arsenic**.

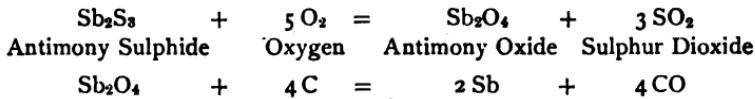
**Marsh's Test for Arsenic.** — Arsenic itself is not poisonous, but its compounds are among the most poisonous substances known. Fortunately, combined arsenic is easily detected by a simple method, called **Marsh's test**. An apparatus for generating hydrogen is provided with a hard glass horizontal delivery tube, narrowed in places and drawn to a point. Pure zinc, pure dilute sulphuric acid, and the arsenic solution are put in the generator. Hydrogen and gaseous hydrogen arsenide (or **arsine** ( $AsH_3$ )) are formed. If this mixture is lighted at the end of the delivery tube, metallic arsenic is deposited as a black coating on cold porcelain held in the flame; or if the tube is heated in front of a narrow place, arsenic is deposited at this point. This deposit dissolves in sodium hypochlorite solution, but a deposit of antimony, similarly produced, does not dissolve. By this delicate test the merest trace of arsenic is readily and positively detected.

## ANTIMONY.

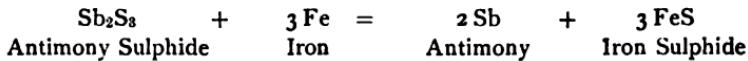
**Occurrence of Antimony.** — Small quantities of free antimony are found. The most common ore is **stibnite** ( $Sb_2S_3$ ), which occurs in Japan, Austria-Hungary, France, Algeria, Italy, Mexico, and Turkey. Large deposits in California and Nevada are now utilized, about 3,000,000 pounds being annually produced.

Stibnite was known in the fifteenth century. The Latin name of antimony is *stibium*, from stibnite, which gives the symbol of the element, Sb.

**Antimony is prepared** on a large scale by two methods. In one the sulphide is roasted, and the oxide thus formed is reduced with charcoal. Equations representing the main changes are —



The other method consists in heating the sulphide with iron, the equation for the chemical change being —



Antimony has interesting **properties**. It is a silver white, crystalline, brittle solid. Its specific gravity is 6.7. At ordinary temperatures antimony does not tarnish in the air, but when heated, it burns with a bluish flame, forming the white, powdery antimony trioxide ( $Sb_2O_3$ ). Powdered antimony burns brilliantly when added to chlorine, bromine, or iodine. Nitric acid oxidizes it, and *aqua regia* dissolves it. Antimony melts at about  $625^{\circ} C$ . It expands on cooling, and is therefore one constituent of type metal (see Alloys of Lead).

**Compounds of Antimony.** — Antimony forms **stibine** ( $SbH_3$ ), which is analogous to ammonia ( $NH_3$ ) and arsine ( $AsH_3$ ), **pyro-** and **meta-acids**, the **oxides**,  $Sb_2O_3$  and  $Sb_2O_4$ , and halogen compounds. It also forms complex compounds in which antimony acts as a metal. **Tartar emetic** is potassium antimonyl tartrate ( $K SbO \cdot C_4H_4O_6$ ). It is used as a medicine and as a mordant in dyeing cotton. **Antimony trisulphide**

( $Sb_2S_3$ ) is a reddish solid, formed by passing hydrogen sulphide gas into a solution of antimony—the test for antimony. The sulphide is used in making the red rubber tubing and stoppers used in the laboratory. The chlorides ( $SbCl_3$  and  $SbCl_5$ ) are formed by the action of chlorine upon the metal; with water they form the white solids called oxychlorides, e.g.  $SbOCl$ . The formation of antimony oxychloride is sometimes used as a test for antimony, but the more common test is the formation of the reddish orange sulphide ( $Sb_2S_3$ ).

#### BISMUTH.

**Bismuth** is usually found in the native state, though it is not abundant nor widely distributed. The oxide ( $Bi_2O_3$ ), or bismite, the carbonate ( $(BiO)_2CO_3 \cdot H_2O$ ), or bismutite, and the sulphide ( $Bi_2S_3$ ), or bismuthinite, are the common ores. The world's supply comes from Saxony.

**Bismuth** is prepared from the native metal by melting it on an inclined plate and allowing it to drain away from the solid impurities. Sometimes the sulphide is roasted, and the resulting oxide is reduced with charcoal, as in the case of antimony.

Bismuth has characteristic properties. It is a grayish white metal with a reddish tinge. Like antimony, it is very brittle. It does not tarnish in dry air, but it grows dull in moist air; and when heated in air it burns with a bluish flame, forming the yellowish oxide ( $Bi_2O_3$ ). Its specific gravity is about 9.9. Hydrochloric acid does not readily attack it, but nitric acid converts it into a nitrate, and hot sulphuric acid into a sulphate.

Bismuth melts at about  $270^{\circ} C.$  But a mixture of bismuth, lead, and tin melts at a low temperature. For example, Newton's metal melts at  $95^{\circ} C.$  and Rose's metal at  $100^{\circ} C.$ ; while Wood's metal, which contains cadmium, melts at only  $66^{\circ} C.$  –  $71^{\circ} C.$  These metallic mixtures are called fusible metals. They are used in making casts of wood cuts; but more often (1) as safety plugs in steam boilers to prevent explosions, (2) as a fuse in electrical apparatus to prevent a short circuit, and (3) to hold in place fireproof doors and the valves in the automatic sprinkling apparatus now placed in large buildings.

**Compounds of Bismuth.**—Bismuth forms no compound with hydrogen. There are three oxides. **Bismuth trioxide** ( $Bi_2O_3$ ) is yellowish.

the **pentoxide** ( $\text{Bi}_2\text{O}_5$ ) is orange red, and the **dioxide** ( $\text{Bi}_2\text{O}_3$ ) is black. Bismuth trioxide is used to fix the gilding on porcelain. The **trichloride** ( $\text{BiCl}_3$ ) is formed by the action of **chlorine** upon bismuth, or by treating bismuth with *aqua regia*. With an excess of water the trichloride forms the **oxychloride** ( $\text{BiOCl}$ ), which is a pearl-white powder, insoluble in water. The formation of the oxychloride is the usual **test for bismuth**. Bismuth, being a metal, forms **hydroxides** ( $\text{Bi(OH)}_3$  and  $\text{BiO} \cdot \text{OH}$ ). **Normal bismuth nitrate** ( $\text{Bi(NO}_3)_3$ ), treated with hot water, forms **basic bismuth nitrate** ( $\text{Bi(OH)}_2\text{NO}_3$  or  $\text{BiONO}_3$ ). The latter, often called **subnitrate of bismuth**, is a white powder used as a medicine for dyspepsia and as a cosmetic.

### EXERCISES.

1. What is the symbol and atomic weight of phosphorus ? Give a brief history of this element. Why is it so named ?
2. Discuss the occurrence of phosphorus.
3. Describe the manufacture of phosphorus (*a*) from a phosphate and sulphuric acid, and (*b*) by the electric method. How is it purified ?
4. Summarize the properties of (*a*) ordinary phosphorus, and (*b*) red phosphorus.
5. Describe briefly (*a*) the oxides of phosphorus, (*b*) orthophosphoric acid, (*c*) metaphosphoric acid, (*d*) pyrophosphoric acid, (*e*) phosphine, (*f*) the phosphorus chlorides.
6. What is (*a*) tricalcium phosphate, (*b*) microcosmic salt, (*c*) "acid phosphate" ?
7. Describe the manufacture of (*a*) sulphur matches, and (*b*) safety matches.
8. Discuss the relation of phosphorus to life.
9. What is a fertilizer ? Name three natural fertilizers. Describe the manufacture of artificial fertilizer. What is a complete fertilizer ?
10. What is the symbol and atomic weight of arsenic ?
11. Name several ores of arsenic. With what metals is arsenic often associated ?
12. Describe the preparation and state the properties of the arsenic.
13. What is the formula of arsenic trioxide ? By what other names is it known ? Summarize its properties. For what is it used ? What is the antidote for arsenic poisoning ?

14. What is (a) Paris green, (b) orpiment, (c) realgar? For what is each used?
15. Describe Marsh's test for arsenic.
16. What is the symbol and atomic weight of antimony?
17. In what forms does antimony occur and where is it found? Describe its preparation. State its chief properties.
18. What is tartar emetic? For what is it used?
19. Describe the test for antimony.
20. What is the symbol of bismuth? How does it occur and where is it found? Describe its preparation. State its properties.
21. State the relation of bismuth hydroxide to bismuth subnitrate. Describe the latter.

#### PROBLEMS.

1. Calculate the percentage composition of (a) sodium phosphate ( $\text{Na}_3\text{PO}_4$ ), (b) dihydrogen phosphate ( $\text{H}_2\text{NaPO}_4$ ), (c) disodium phosphate ( $\text{HNa}_2\text{PO}_4$ ), (d) microcosmic salt ( $\text{HNaNH}_4\text{PO}_4$ ).
2. How much phosphorus is needed to remove the oxygen from a liter of air? (Assume (1)  $2 \text{P} + 5\text{O} = \text{P}_2\text{O}_5$  and (2) air is 20 per cent oxygen.)
3. How much phosphorus is there in a ton (2000 lb.) of bone ash ( $\text{Ca}_3(\text{PO}_4)_2$ )?
4. If a skeleton weighs 25 lb. and contains 60 per cent calcium phosphate, how much phosphorus does it contain?
5. What is the weight of a cylindrical stick of ordinary phosphorus 10 cm. long and 15 mm. in diameter? (Suggestion.—What is the specific gravity of phosphorus?)
6. Calculate the percentage composition of (a) orpiment ( $\text{As}_2\text{O}_3$ ), (b) realgar ( $\text{As}_2\text{S}_3$ ), (c) white arsenic ( $\text{As}_2\text{O}_3$ ).
7. What is the weight of a piece of antimony 25 cm. long, 15 cm. wide, and 2 mm. thick?

## CHAPTER XX.

### **METALS.**

**Introduction.**—The elements studied thus far are chiefly non-metals. Metals, however, have been mentioned, and many of their properties have been discussed. It is the purpose of the present chapter to review these properties and prepare the way for a fuller treatment of the metals.

**Metals and Non-metals.**—Many years ago the chemical elements were divided into two classes, called *metals* and *non-metals*. The division was based largely on the physical properties of the elements. The opaque, lustrous, more or less heavy, hard, ductile, malleable, tenacious solids were called **metals**. All gases and the solids such as carbon, sulphur, phosphorus, and iodine were called **non-metals**. No such sharp dividing line, however, can be drawn between metals and non-metals. Some, of course, have pronounced properties, like the non-metal sulphur and the metal iron. These are typical. But a few have variable properties. Sometimes they act as metals and at other times as non-metals. Antimony and arsenic belong to this border-line class ; they are sometimes called the **metalloids**. The classification into metals and non-metals is no longer accurate, but it is very convenient. The use in common life of the words *metallic* and *metal* seldom leads to confusion.

**Properties of Metals.**—The physical properties of metals are familiar, though variable between wide limits.

All have a **metallic luster**, *i.e.* the marked property of reflecting light from their polished or untarnished surfaces.

All are **opaque** except when in very thin films. The color of many is white, though the tint varies. Thus silver, sodium, aluminium, mercury, magnesium, iron, and tin are nearly pure white, and bismuth is reddish white. Copper is the only red metal, and gold the only yellow one, which is an element. Most metals are **malleable** and **ductile**, *i.e.* they may be hammered or rolled into sheets and drawn into wire. Gold, copper, silver, iron, platinum, and aluminium possess both these properties to a marked degree; while lead, zinc, and tin are very malleable though not so ductile. Antimony and bismuth are **brittle**. The **hardness** of metals varies. At the ordinary temperature mercury is a liquid, sodium and lead can be cut easily with a knife, and so on through the list up to iridium, which is as hard as steel. In **specific gravity**, which was once thought to be very high, the metals range between lithium, which has the specific gravity 0.534, and osmium, which has the specific gravity 22.48. Sodium and potassium also are lighter than water, while magnesium has the specific gravity 1.75, and aluminium 2.58. Metals are good **conductors of heat and electricity**. They also vary in this property. Silver, copper, and aluminium are the best conductors, and have therefore many practical applications. Bismuth is the poorest conductor.

The distinctive property of metals is not physical, but chemical. Metals form oxides which dissolve in water and produce bases. Metals are the characteristic elements of bases. On the other hand, non-metals form acid-producing compounds.

**Occurrence of Metals.**— Only a few metals are found free in the earth's crust, and these are seldom pure. Of

the six metals known to the ancients, — gold, copper, silver, tin, iron, and lead, — only gold and copper are found free. The solid elements and their compounds which occur in the earth's crust are called **minerals**. And those minerals from which metals can be profitably extracted are called **ores**. The most abundant classes of ores are oxides, sulphides, carbonates, and hydroxides. Lead, zinc, mercury, and silver sulphides are abundant. Besides native copper, the sulphide and carbonate are found. Iron occurs as oxide, carbonate, hydroxide, and sulphide. Many ores contain arsenic. Some ores are very complex.

**Preparation of Metals.** — The series of operations by which useful metals are extracted from their ores is called **metallurgy**. It includes preliminary treatment, smelting, electrolysis, refining, and other operations necessary to change the ore into a metal ready for manufacture into useful articles. The object of the **preliminary treatment** is to prepare the ore for smelting or for a similar operation by which the metal is obtained in a state adapted for further purification or refining. The ore as it comes from the mine is usually mixed with earthy matter or rock called **gangue**. This impurity is removed by mechanical or chemical processes, sometimes by both. The mechanical process illustrates one kind of preliminary treatment. The ore is first crushed in a **stamp mill**. This is a huge, heavy mortar and pestle. The pestle or stamp falls repeatedly upon the ore, which is slowly fed into the mortar or die. A current of water (or air) forces the fine particles out of the mortar through a sieve. The lighter particles of the impurities are washed away, and the metallic grains are extracted by another mechanical operation, though chemical processes are frequently employed, especially with inferior ores. This separation of the valuable part

of the ore from the gangue, and reducing it to a smaller bulk is often called **ore dressing** or **concentration**. Copper is extracted from the Lake Superior ores mainly by this method of preliminary treatment.

Gold and silver ores are treated this way, and then extracted from the slime by mercury. The latter operation is called **amalgamation**. The most common method of extracting metals from their ores is by **smelting**. The process varies with the kind and composition of the ore. Essentially, it consists in heating a mixture of the ore and coke (or coal) in a furnace. The ores used must, as a rule, be oxides. Sulphides, hydroxides, and carbonates are first roasted or **calcined** to convert them into oxides. The essential chemical change in smelting is a reduction of the oxide by the carbon. The carbon and oxygen unite and pass off as a gas, leaving the metal to run out at the bottom. Limestone, or a similar substance, called a **flux**, is added to the mixture, if necessary, to facilitate the melting and to assist in removing the impurities as a glassy substance, called **slag**. The operation is conducted in different kinds of furnaces. Iron, for example, is smelted in a huge upright furnace called a **blast furnace** (Fig. 72), because a current of air is forced through the melted mass to facilitate the fusion and chemical changes. In such a furnace the fuel and ore are in direct contact. When this is undesirable, the **reverberatory furnace** is used (Fig. 54). As the figure shows, in this furnace the flame is reflected or reverberated upon the ore under treatment. In this kind of furnace the ore may be oxidized or reduced without coming in contact with the fuel. Some ores demand special methods, which will be described in connection with these metals. **Electrolysis** is used to extract some metals, especially aluminium. Other metals, notably

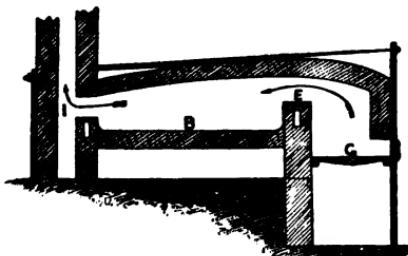


FIG. 54.—Reverberatory furnace. The fire burns on the grate, *G*, and the long flame which passes over the bridge, *E*, is reflected down by the sloping roof upon the contents of the furnace. Gases escape through *I*. The charge, which rests upon *B*, does not come in contact with the fuel, but is oxidized or reduced by the flame.

copper, are purified by electrolysis. A few metals are extracted by a wet process. That is, the ores are dissolved, and the metal is precipitated by adding some substance or by electrolysis. Thus, inferior gold ores are dissolved by treatment with potassium cyanide, and the gold is then precipitated by zinc.

**Alloys** are mixtures or compounds of two or more metals. Some fused metals mix in all proportions, while others seem to form definite compounds. The properties of alloys vary with the constituents and their properties. Some alloys, especially those of copper and of lead, have many industrial uses. Alloys in which mercury is a constituent are called **amalgams**.

#### EXERCISES.

1. Define the terms *metal* and *non-metal* as they are ordinarily used. Name six or more examples of each class. Define and illustrate the term *metalloid*. Why is this classification inaccurate?
2. State the familiar physical properties of metals. Define (*a*) metallic luster, (*b*) malleable, (*c*) ductile, (*d*) specific gravity.
3. How does the color of metals differ from their luster? Name five metals which are white. What color has (*a*) gold, (*b*) copper, (*c*) zinc, (*a*) lead, (*e*) iron?
4. What metals are brittle? Malleable? Soft? Hard? Heavy? Light? What metals conduct electricity well?
5. What is the distinctive chemical property of metals? Of non-metals? Illustrate your answer.

6. What metals are often found free in nature? Define and illustrate the terms (*a*) *mineral*, and (*b*) *ore*. What are the most abundant classes of ores?

7. What metals occur abundantly as (*a*) sulphides, (*b*) oxides, (*c*) carbonates?

8. Define metallurgy. What general operations does it include?

9. What is the object of the preliminary treatment of ores? How is it accomplished mechanically? Define (*a*) gangue, (*b*) concentration, (*c*) amalgamation. What metal is often extracted (*a*) mechanically, (*b*) by amalgamation?

10. Define smelting. What fundamental chemical change does it usually involve? Define and illustrate (*a*) calcination, (*b*) flux, (*c*) slag.

11. Describe (*a*) a reverberatory furnace, and (*b*) a blast furnace. What is their essential difference?

12. What is the wet process of extracting ores?

13. What are (*a*) alloys, (*b*) amalgams?

#### PROBLEMS.

1. What is the specific gravity of gold, if a piece weighs 4.676 gm. in air, and loses 0.244 gm. when weighed in water? (Note.— Specific gravity equals the weight in air divided by the loss of weight in water.)

2. A piece of aluminium weighs 150 gm. in air and 75 gm. in water. What is its specific gravity?

3. A piece of iron weighs 292.8 gm. in air and 255.3 gm. in water. What is its specific gravity?

4. A piece of copper weighing 50 gm. in air lost 5.6 gm. when weighed in water. What is its specific gravity?

5. A piece of lead pipe weighs 158.9 gm. in air and 144.9 gm. in water. Calculate the specific gravity.

## CHAPTER XXI.

### SODIUM, POTASSIUM, AND LITHIUM.

**Introduction.**—Sodium and potassium, and the rare elements lithium, rubidium, and caesium, form a natural group, known as the **alkali metals**. The different elements and their corresponding compounds resemble each other closely.

Sodium and potassium were discovered by Sir Humphry Davy in 1807 by the electrolysis of their hydroxides. Bunsen, by means of the spectroscope, discovered lithium in 1855, caesium in 1860, and rubidium in 1861.

#### SODIUM.

**Occurrence.**—Sodium is not found free. Sodium chloride and sodium nitrate are the most abundant compounds. Many rocks, plants, and mineral waters contain combined sodium. About 2.5 per cent of the earth's crust is sodium.

The symbol of sodium, Na, is from the Latin word *natrium*, which in turn comes from the Greek word *natron*, an old name of sodium carbonate.

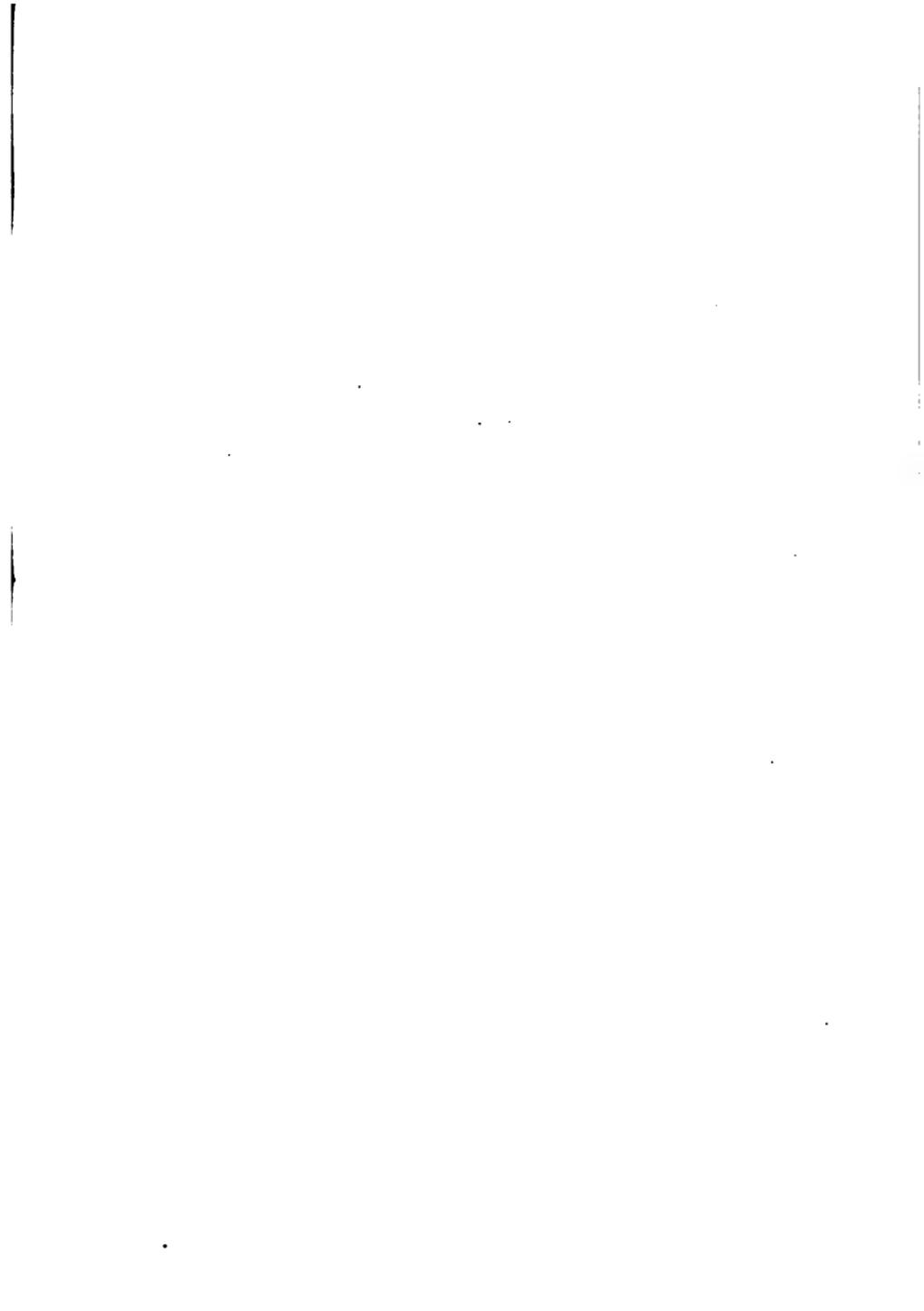
**Preparation.**—Sodium is now manufactured on a large scale by the electrolysis of fused sodium hydroxide. This method was used by Davy in 1807 to isolate sodium, but its commercial success was only recently made possible by Castner. Figure 55 is a sketch of the apparatus used. The body of the steel cylinder, S, rests within a heated flue. Hence the sodium hydroxide is solid in the neck, B, and serves to protect the joint made by the iron cathode,



SIR HUMPHREY DAVY

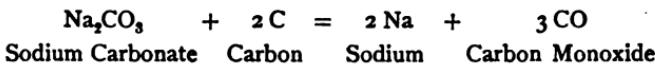
1778-1829

THE FAMOUS ENGLISH CHEMIST WHOSE BRILLIANT DISCOVERIES HAVE NEVER BEEN  
SURPASSED

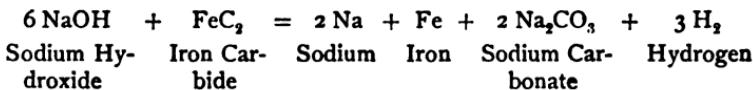


*C*, and the crucible. *A, A* is the iron anode. A collecting pot, *P*, dips into the molten caustic soda. As the electrolysis proceeds, the sodium formed at *C* collects in *P*, and a wire gauze, *G, G*, keeps it from mixing with the caustic soda. The sodium is ladled out at intervals from *P*. The hydrogen, which is liberated, accumulates also in *P* and prevents the sodium from oxidizing. The hydrogen sometimes escapes and explodes.

Sodium was formerly manufactured by two methods. (1) Sodium carbonate and carbon heated to a high temperature change thus—



The mixture was heated in iron retorts, and the sodium vapor, in passing through a flat iron receiver, condensed to a liquid, which was collected under paraffin or mineral oil. (2). The other chemical method, devised by Castner in 1886, consisted essentially in heating sodium hydroxide with a mixture of iron and carbon. Probably iron carbide was the essential reducing agent, and the change might be represented thus—



**Properties.**—Sodium is a silver-white metal. It is so soft that it may be easily molded with the fingers and cut with a knife. It floats upon water, since its specific

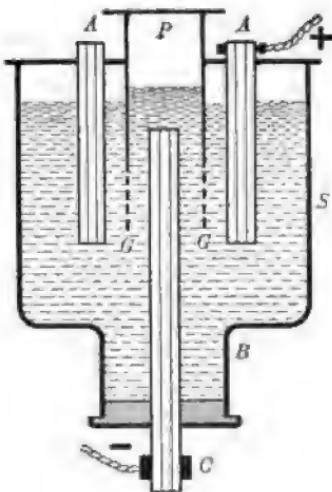
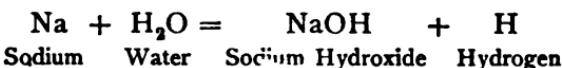


FIG. 55.—Apparatus for the manufacture of sodium by the electrolysis of sodium hydroxide.

gravity is only .971. Heated in the air, it melts at 96° C., and at a higher temperature it burns with a brilliant yellow flame, forming sodium peroxide ( $\text{Na}_2\text{O}_2$ ). This intense yellow color is characteristic of sodium and is the usual test for the element (free or combined). In moist air the bright surface quickly tarnishes, and sodium as usually seen has a brownish coating. It is, therefore, kept under kerosene or a liquid free from water. It decomposes water at ordinary temperatures, liberating hydrogen and forming sodium hydroxide, thus —



If held in one place upon water by filter paper, enough heat is generated to set fire to the hydrogen, which burns with a yellow flame, owing to the presence of volatilized sodium (see Interaction of Sodium and Water, Ch. I, "er V). If melted sodium is put into chlorine, the two elements combine with a brilliant flame, forming sodium chloride. It was in this way that Davy, in 1810, proved that common salt is really nothing but sodium chloride. It combines directly with the other halogens.

A molecule of sodium contains only one atom.

**Sodium** is used in the laboratory to extract water from alcohol and ether and to prepare organic compounds. Large quantities are consumed in the manufacture of sodium peroxide ( $\text{Na}_2\text{O}_2$ ) and sodium cyanide ( $\text{NaCN}$ ). Its power to reduce oxides gives it limited use in preparing certain metals, e.g. magnesium.

**Sodium Chloride**,  $\text{NaCl}$ , is the most important compound of sodium. It is familiar under the name of **salt** or **common salt**. The presence of salt in the ocean, in lakes and springs, and in the soil is mentioned in the oldest historical records. It is one of the most abundant substances. The sources of salt are sea water, rock salt, and brines.

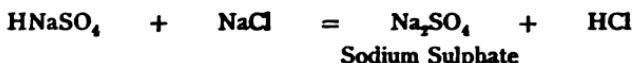
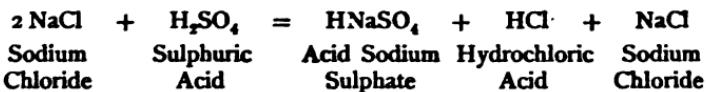
**Preparation of Salt.**—Sea water contains nearly 4 per cent of salts, and three fourths of this amount is sodium chloride. (1) In warm countries, as on the shores of the Mediterranean Sea, shallow ponds of sea water near the shore are evaporated by exposure to the sun and wind, and the salt is collected. (2) In some regions sea water is first concentrated by allowing it to trickle over heaps of brush and then evaporated to crystallization in shallow pans. (3) In cold countries, as on the shores of the White Sea in Russia, sea water is allowed to freeze and the ice is removed. The ice contains no salt, so the operation is repeated until the remaining liquid becomes strong enough to evaporate profitably over a fire. (4) Deposits of salt are found in many parts of the globe, the most important being in England, Austria-Hungary, and Germany. In these regions and some parts of the United States, the salt is mined and purified like other minerals. This variety is coarse and often impure, and is largely used in curing meat and preserving hides. (5) Most of the salt produced in the United States is obtained from natural or artificial brines, *i.e.* from strong solutions of salt. Artificial brines are made by forcing water into salt deposits. Brines are obtained in New York, Michigan, Kansas, Ohio, West Virginia, California, Utah, and Louisiana. They are evaporated in vats by the sun's heat or by heating in kettles or pans.

All these methods give a product containing as impurities salts of sodium, calcium, and magnesium, which are largely removed by further special treatment. The dampness of salt is due mainly to the magnesium chloride it contains (see Deliquescence, Chapter IV).

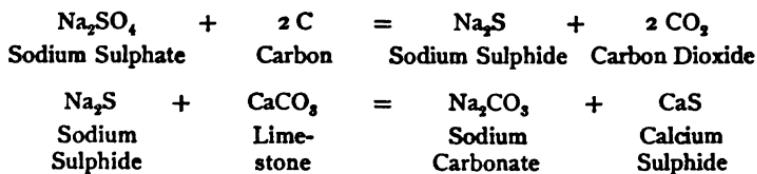
**Properties and Uses of Salt.**—Salt is soluble in water, 100 gm. of water dissolving about 36 gm. of salt at 0° C., and 40 gm. at 100° C. It crystallizes in cubes. This substance is an essential ingredient of the food of man and animals. Besides its universal domestic use, enormous quantities are consumed in the preparation of many sodium compounds, particularly sodium carbonate (see below), of hydrochloric acid and bleaching powder. The annual production of salt in the United States is over 3,000,000 tons, while over 200,000 tons are imported. This is about the average consumption.

**Sodium Carbonate**,  $\text{Na}_2\text{CO}_3$ , is next to sodium chloride in importance. Small quantities of hydrated sodium carbonates are found in Egypt, Russia, and in California and Nevada. Formerly it was obtained from the ashes of marine plants, but sodium chloride is now the source. The manufacture of sodium carbonate is one of the most extensive chemical industries. Two processes are used, the Leblanc and the Solvay.

The Leblanc Process has three steps. (1) Sodium chloride is changed into sodium sulphate by sulphuric acid, the two equations for the changes being —



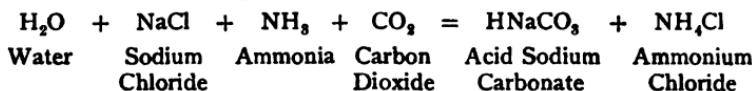
This operation is called the "salt cake process"; the impure product, called "salt cake," contains about 95 per cent of sodium sulphate. The hydrochloric acid is a by-product (see Hydrochloric Acid). (2) The sodium sulphate is changed into sodium carbonate by heating the "salt cake" with coal and limestone, the main changes being represented by the equations —



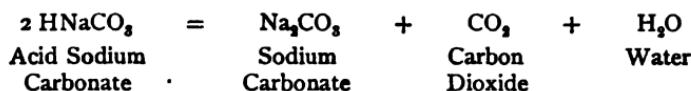
This operation is called the "black ash process." The product is a dark brown or gray porous mass, and contains, besides 37 to 45 per cent of sodium carbonate, considerable calcium sulphide and other impurities. The calcium sulphide is a source of sulphur (see Sulphur). (3) The sodium carbonate is rapidly separated from the insoluble portions of the "black ash" by extraction with a regulated stream of water. The solution of sodium carbonate thus obtained is evaporated to crys-

tallization, and the crude crystals are ignited. This product is known as **soda ash**, and from its solution in water are obtained **soda crystals** or **sal soda** ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ ).

The **Solvay Process**, often called the **ammonia-soda process**, consists in saturating a cold concentrated solution of sodium chloride first with ammonia gas and then with carbon dioxide gas. The equation for the chemical change is —



The acid sodium carbonate is nearly insoluble in the cold ammonium chloride solution, and therefore separates. It is changed, by heating, into sodium carbonate, thus —



The liberated carbon dioxide is used again, and from the ammonium chloride the ammonia is recovered and also used.

**Properties and Uses of Sodium Carbonate.**—Crystallized sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ ) is often called **alkali** or **soda**. It loses water in the air, becoming dull at first and finally falling to a powder. When heated, it melts in its water of crystallization, and continued heating changes it into the white anhydrous salt ( $\text{Na}_2\text{CO}_3$ ). It is soluble in water, and the alkaline solution is used as a cleansing agent; hence the name **washing soda**.

The alkalinity of sodium carbonate solution is due to hydrolysis. Sodium carbonate ionizes into  $2 \text{Na}^+$  and  $\text{CO}_3^{2-}$ , but the unstable  $\text{CO}_3$ -ions form  $\text{HCO}_3$ -ions with the H-ions from the slightly dissociated water. This removal of H-ions finally leaves in the solution sufficient OH-ions to produce alkalinity.

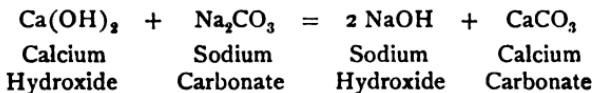
**Sodium Bicarbonate**,  $\text{HNaCO}_3$ , is a by-product of the Solvay process, and it may also be prepared by treating crystallized sodium carbonate with carbon dioxide gas. It is a white powder, less soluble in water than the normal

carbonate. When heated or when mixed with an acid or an acid salt, sodium bicarbonate gives up carbon dioxide. This property early led to its use in cooking, and gives the names **cooking soda**, **baking soda**, or simply **soda**.

Sodium bicarbonate is one ingredient of **baking powder** and of the various mixtures (except yeast) used to raise bread, cake, and other food. Since cream of tartar is slightly acid, it is usually used to liberate the gas. Sour milk, which contains lactic acid, is sometimes used in place of cream of tartar. When pastry is raised with soda and cream of tartar, the escaping carbon dioxide puffs up the dough. Hence baking soda is often called **saleratus** — the salt which aerates (from the Latin words *sal*, salt, and *aer*, air or gas). Effervescent powders, such as Seidlitz (or Rochelle) and soda powders, contain sodium bicarbonate in one paper and tartaric acid or one of its acid salts in the other. When these are mixed in water, carbon dioxide is liberated. Sodium bicarbonate is used as a medicine to neutralize an acid stomach. For example, the "soda mints" sometimes taken for this purpose are mainly sodium bicarbonate.

**Sodium Hydroxide or Caustic Soda**, NaOH, is a white corrosive solid. It absorbs water and carbon dioxide rapidly from the air. It dissolves readily in water, with rise of temperature, and the solution is strongly alkaline. It melts easily, and is often cast into sticks for use in the laboratory. Immense quantities are used in making hard soap, paper, and dyestuffs; in bleaching, and in refining kerosene oil.

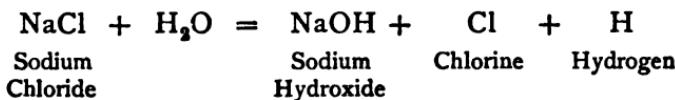
Sodium hydroxide was formerly manufactured by treating sodium carbonate with calcium hydroxide. Lime is added to a boiling, dilute solution of soda ash, and the main change is represented thus —



The solution of sodium hydroxide is separated from the insoluble calcium carbonate, and concentrated by heating in iron kettles to the de-

sired strength or until the mass becomes stiff. Air is then blown in or sodium nitrate added to oxidize sulphides to sulphates. After standing several hours to allow other impurities to settle, the caustic soda is put into iron barrels called drums. It solidifies on cooling, and the drums are at once sealed to keep out the air.

Sodium hydroxide is now manufactured on a large scale at Niagara Falls, New York, by the **electrolysis of sodium chloride**, according to the equation —



The apparatus is shown in Figure 56. The carbon anodes (*A*, *A*) pass into the outer compartments which contain brine, and the iron cathodes into the middle compartment which contains sodium hydroxide solution. When the cur-

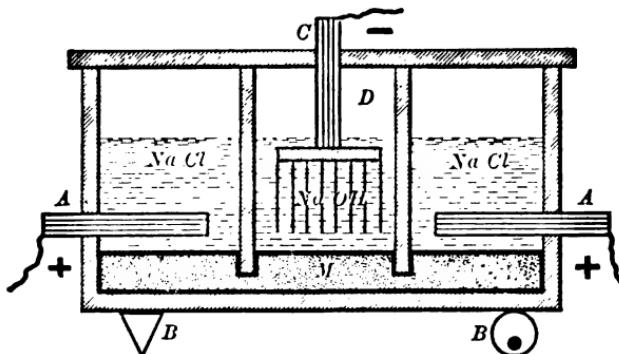


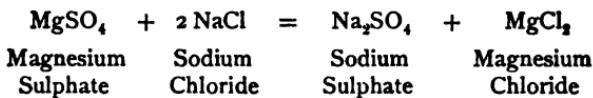
FIG. 56.—Apparatus for the manufacture of sodium hydroxide by the electrolysis of sodium chloride.

rent passes, chlorine is evolved at the anodes and flows out through pipes (not shown), and sodium is produced on the surface of the mercury (*M*) which covers the floor of the whole apparatus. The sodium forms an amalgam

with the mercury, and by rocking the apparatus on the device, *B*, *B*, the sodium amalgam flows into the compartment, *D*, where the sodium is liberated by the action of the electric current, which passes between the cathode and the amalgam. The sodium reacts with the water forming hydrogen, which passes off through pipes (not shown) and **sodium hydroxide**, which flows into a special tank. Both the chlorine and sodium hydroxide are nearly pure. The solution of caustic soda is finally treated, if necessary, as in the older process.

**Sodium Sulphate**,  $\text{Na}_2\text{SO}_4$ , is one of the products obtained in the manufacture of sodium carbonate (see above).

In another method, sulphur dioxide, steam, and air are passed into hot sodium chloride. And at Stassfurt, magnesium sulphate and sodium chloride are allowed to interact in the cold, thus —



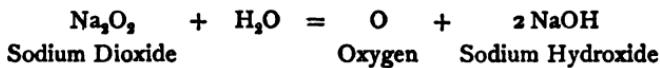
Sodium sulphate is a white anhydrous solid. It dissolves readily in water, and when a strong solution made at  $30^\circ\text{C}$ . is cooled, large transparent bitter crystals separate. They have the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and are called **Glauuber's salt**, from the discoverer. They lose water when exposed to air, and the salt continues to effloresce until it becomes an anhydrous powder. The crude salt is used in the glass and dyeing industries, and the purified salt as a medicine.

**Sodium Nitrate**,  $\text{NaNO}_3$ , is found abundantly in Chili, and is often called **Chili saltpeter**. It is a white solid, which becomes moist in the air. Large quantities are used as a fertilizer, either alone or mixed with compounds of

potassium and of phosphorus, and for making nitric acid and potassium nitrate.

The natural deposits are in a dry region near the coast and cover over 200,000 acres. Chili controls the industry, and exports annually over a million tons. The crude salt, which looks like rock salt, is purified by crystallization into a product containing 94-98 per cent of the nitrate. The final mother liquor is a source of iodine (see Iodine).

**Sodium Dioxide or Peroxide**,  $\text{Na}_2\text{O}_2$ , is a yellowish solid. It is used to bleach straw and delicate fabrics. With water it liberates oxygen, according to the equation —



**Miscellaneous.** — Sodium cyanide ( $\text{NaCN}$ ) is used to extract gold from poor ores. Sodium monoxide ( $\text{Na}_2\text{O}$ ) is a grayish solid. The sodium phosphates, sodium thiosulphate, acid sodium sulphite, sodium silicate, and sodium tetraborate or borax have been described.

#### POTASSIUM.

**Occurrence.** — This metal is not found free, but its compounds are abundant. The minerals mica and feldspar are silicates containing potassium. By the decay of these and other minerals, potassium compounds find their way into the soil, thence into plants and animals. Potassium salts are found in wood ashes, in suint, — the oily substance washed from sheep's wool, — in beet-sugar residues, and in the deposits in wine casks. Sea water and mineral waters contain potassium salts, particularly potassium chloride and potassium sulphate. Many potassium salts are found at Stassfurt. About 2.5 per cent of the earth's crust is potassium.

The Stassfurt deposits of the salts of potassium and other metals are near Magdeburg, Germany. About 16 different salts make up the beds, which are nearly 5000 feet thick. The deposits were doubtless formed by the evaporation of sea water, though the different simpler

salts interacted, forming complex ones. The most important salts are —

- Kainite . . . . KCl, MgSO<sub>4</sub> · 3 H<sub>2</sub>O.
- Carnallite . . . KCl, MgCl<sub>2</sub> · 6 H<sub>2</sub>O.
- Polyhalite . . . K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, 2 CaSO<sub>4</sub> · 2 H<sub>2</sub>O.
- Sylvite . . . . KCl.
- Picromerite . . K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub> · 6 H<sub>2</sub>O.

The name *potassium* comes from the word *potash*. The symbol, K, is from *kalium*, the Latin equivalent of *kali*, which is derived from an Arabic term for an alkaline substance.

**Preparation.** — Potassium is now obtained by the electrolysis of potassium hydroxide. Formerly it was manufactured, like sodium, by heating to a high temperature a mixture of potassium carbonate and carbon or of potassium hydroxide and iron carbide (see under Sodium).

**Properties.** — Like sodium, potassium is a soft, silver-white metal, light enough to float upon water — the specific gravity being 0.86. Its brilliant luster soon disappears in air, owing to rapid oxidation. Potassium as ordinarily seen is, therefore, covered with a grayish coating, and, like sodium, must be kept under mineral oil. It melts at 62.5° C., and at a higher temperature burns with a violet-colored flame. This color is characteristic of burning potassium, and is a **test for the metal** and its compounds. Like sodium, it decomposes water at ordinary temperatures, though more energetically. The heat evolved immediately ignites the hydrogen, and the melted potassium surrounded by a violet flame dashes to and fro upon the cold water. The main reaction corresponds to the equation —



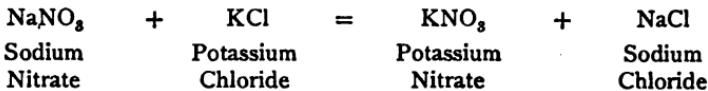
Potassium combines with the halogens and other elements more vigorously than sodium, and forms analogous compounds.

**Potassium Chloride**, KCl, is found native in the Stassfurt deposits. It is also obtained in large quantities by decomposing carnallite and crystallizing the potassium chloride from the more soluble magnesium chloride. It is a white solid which crystallizes in cubes and otherwise resembles sodium chloride. It is used chiefly to prepare other potassium salts, especially the nitrate and chlorate.

Potassium bromide and potassium iodide have been described (see Chapter XVI).

**Potassium Nitrate**, KNO<sub>3</sub>, is also called **niter** and **salt-peter**. It is formed in the soil of many warm countries by the decomposition of nitrogenous organic matter (see Nitrification).

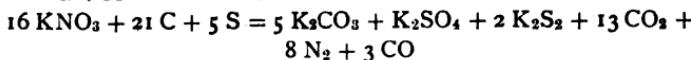
It is now made by mixing hot, concentrated solutions of native sodium nitrate and potassium chloride, which interact thus —



The sodium chloride, being less soluble, separates, and is removed. By evaporation, small crystals of potassium nitrate, called "niter meal," are obtained, and further purified by recrystallization.

Potassium nitrate is a white solid. It dissolves easily in cold water with a fall of temperature, and very freely in hot water, but it is not hygroscopic. It is crystalline, but contains no water of crystallization. The taste is salty and cooling. It melts at 339° C., and further heating changes it into **potassium nitrite** ( $\text{KNO}_2$ ) and oxygen. At a high temperature, potassium nitrate gives up oxygen readily, especially to charcoal, sulphur, and organic matter. This oxidizing power leads to its extensive use in making gunpowder, fireworks, matches, explosives, and in many chemical operations.

**Gunpowder** is a mixture of potassium nitrate, charcoal, and sulphur. The ingredients are first purified, pulverized, and thoroughly mixed. This mixture is pressed, while damp, into a thin sheet; and the "press cake" thus formed is broken into small grains, which are sorted by sieves. The grains are then smoothed or "glazed" by rolling them in a barrel, again sifted, and finally dried at a low temperature. The proportions differ with the use of the powder. The United States army standard black powder contains 75 per cent of potassium nitrate, 15 of charcoal, and 10 of sulphur. When gunpowder burns in a closed space, a large volume of gas is suddenly formed. So enormously is this gas expanded by the heat that it would fill several hundred times the space taken by the powder itself. The pressure exerted by this expanding gas is many tons. It is this pressure which forces the ball from a cannon and tears a rock to pieces. The chemical changes attending the explosion of gunpowder in a closed space are complex, as may be seen by the following (approximate) equation:—



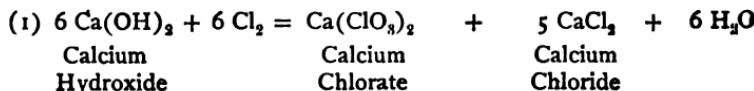
Probably secondary reactions produce other gases besides carbon dioxide and nitrogen.

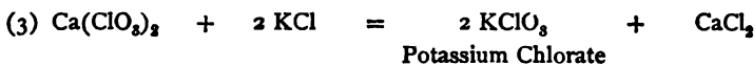
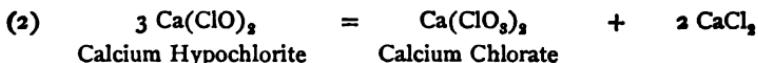
**Potassium Chlorate**,  $\text{KClO}_3$ , is a white, crystallized, lustrous solid. It tastes like potassium nitrate. It melts at  $334^\circ \text{C}$ . and at a high temperature decomposes into oxygen and potassium chloride as final products, thus—



It is used to prepare oxygen, and in the manufacture of matches and fireworks. In the form of "chlorate of potash tablets" it is used as a remedy for sore throat.

Potassium chlorate is manufactured by passing chlorine into calcium hydroxide (milk of lime) and adding potassium chloride to the mixture. The simplest equations for the complex changes may be written thus:—





The salt is also made by the electrolysis of a hot solution of potassium chloride, though it has been found more satisfactory to first prepare sodium chlorate and convert this salt into potassium chlorate by potassium chloride.

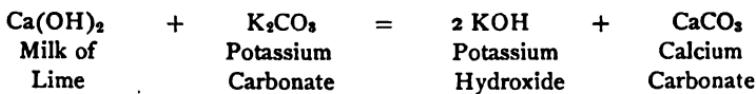
**Potassium Carbonate**,  $\text{K}_2\text{CO}_3$ , is a white solid. It deliquesces in the air, is very soluble in water, and the solution has a strong alkaline reaction. It was formerly obtained by treating wood ashes with water, and evaporating the solution to dryness. The crude salt thus obtained has long been called **potash**, and a purer product is known as **pearlash**. (The term *potash* is sometimes applied to potassium oxide,  $\text{K}_2\text{O}$ .) It is used extensively in the manufacture of hard glass, soft soap, caustic potash, and other potassium compounds.

Potassium carbonate is obtained from suint by igniting the greasy mass and extracting the potassium carbonate with water. Beet-sugar residues also furnish potassium carbonate. After the sugar has been obtained from the beet sirup, the molasses is changed by fermentation into alcohol, which is distilled off; the liquid residue is evaporated to dryness and ignited, and the potassium carbonate extracted with water. Pure potassium carbonate is prepared by igniting cream of tartar made from the deposits in wine casks. All these sources emphasize the intimate relation of potassium compounds to vegetable and animal life. The bulk of the potassium carbonate is now made from potassium sulphate or from the chloride by the Leblanc process, owing to the abundance of crude potassium salts at Stassfurt.

**Potassium Hydroxide or Caustic Potash**,  $\text{KOH}$ , is a white brittle solid, resembling caustic soda. It absorbs water and carbon dioxide very readily; and if exposed to the air, soon becomes a thick solution of potassium

carbonate. Like sodium hydroxide, it dissolves in water with evolution of heat, forming a strongly alkaline, caustic solution. It is one of the strongest bases, even glass and porcelain being corroded by it. Besides its use in the laboratory, large quantities are consumed in making soft soap.

Potassium hydroxide was formerly made in the same way as sodium hydroxide, viz. by adding lime or milk of lime to a boiling dilute solution of potassium carbonate, the equation for the change being :—



It is now made by the electrolysis of a solution of potassium chloride.

**Miscellaneous.** — **Potassium Cyanide** ( $\text{KCN}$ ) is a white solid, very poisonous, very soluble in water, and having an odor like bitter almonds (see Cyanogen, Chapter XIV). **Potassium Sulphate** ( $\text{K}_2\text{SO}_4$ ) is manufactured from kainite, and is largely used as a fertilizer and in making potassium carbonate.

**Relation of Potassium to Life.** — Potassium, like nitrogen and phosphorus, is essential to the life of plants and animals. The ash of many common grains, vegetables, and fruits contains potassium as the carbonate. Potassium salts are supposed to assist in the formation of starch, just as phosphorus is indispensable to the transformation of nitrogen compounds. Potassium salts taken from the soil by plants must be returned if the soil is to be productive. Sometimes crude kainite is used extensively as a fertilizer; but wood ashes, or the sulphate and chloride, are often used to supply potassium salts.

**Lithium**, Li, is a silver-white metal and has the specific gravity of only .534. It is the lightest of the metallic elements. Its compounds are widely distributed in small quantities in minerals, mineral waters, and plants. Lithia water and citrate of lithium are often prescribed as a remedy for diseases of the kidneys. Lithium compounds color the Bunsen flame bright red — a delicate test for the metal.

Rubidium and Cæsium, Rb and Cs, have properties and form compounds analogous to those of potassium.

### EXERCISES.

1. Name the alkali metals. What is the symbol of each? When and by whom was each discovered?
2. What are the important compounds of sodium? What per cent of the earth's crust is sodium?
3. Describe the manufacture of sodium by electrolysis. Describe the older methods of manufacture.
4. Summarize (*a*) the physical properties, and (*b*) the chemical properties of sodium. How is it usually kept? For what is it used?
5. Discuss the interaction of sodium and water (see Chapter V).
6. Give the chemical name and formula of common salt. Where is it found?
7. Describe the different methods of preparing salt. State (*a*) the properties, and (*b*) the uses of salt.
8. Discuss the manufacture of sodium carbonate by (*a*) the Leblanc process. (*b*) By the Solvay process.
9. What is (*a*) soda, (*b*) soda ash, (*c*) salt cake, (*d*) soda crystals, (*e*) sal soda, (*f*) washing soda, (*g*) "alkali"?
10. State the properties and uses of sodium carbonate.
11. Describe the preparation, and state (*a*) the properties, and (*b*) the uses of sodium bicarbonate.
12. What is (*a*) acid sodium carbonate, (*b*) saleratus, (*c*) baking powder, (*d*) baking soda, (*e*) caustic soda?
13. State the properties and uses of sodium hydroxide.
14. Describe the manufacture of sodium hydroxide (*a*) from lime and sodium carbonate, and (*b*) by electrolysis of sodium chloride.
15. How is sodium sulphate manufactured? State its properties and uses.
16. Where is sodium nitrate found? State its properties and uses.
17. Review briefly (*a*) sodium thiosulphate, (*b*) water glass, (*c*) borax.
18. What is a simple test for (*a*) sodium, and (*b*) potassium?
19. Give the formula of (*a*) sodium carbonate, (*b*) sodium chloride, (*c*) sodium sulphate, (*d*) sodium hydroxide, (*e*) sodium bicarbonate, (*f*) Glauber's salt, (*g*) sodium nitrate.

20. Discuss the occurrence of potassium compounds.
21. Discuss the Stassfurt deposits.
22. How is potassium prepared? State (a) its physical properties, and (b) its chemical properties.
23. Describe the interaction of potassium and water.
24. Describe the preparation, and state the properties and uses of (a) potassium chloride, and (b) potassium nitrate.
25. Compare potassium nitrate and potassium nitrite..
26. Describe the manufacture of gunpowder. Upon what does its use depend?
27. State the properties and uses of (a) potassium chlorate, (b) potassium carbonate, (c) potassium hydroxide.
28. Describe the manufacture of (a) potassium chlorate, (b) potassium carbonate, (c) potassium hydroxide.
29. What is (a) potash, (b) pearlash, (c) chlorate of potash?
30. Discuss the relation of potassium to life.
31. State the derivation of the names (a) sodium, and (b) potassium.
32. What is (a) niter, (b) saltpeter, (c) Chili saltpeter?
33. What is the formula of the following compounds of potassium: (a) hydroxide, (b) carbonate, (c) nitrate, (d) nitrite, (e) sulphate, (f) chlorate, (g) cyanide?
34. Describe lithium. For what are its compounds used?

### PROBLEMS.

1. How much potassium carbonate is necessary to prepare a kilogram of potassium hydroxide? (Assume  $K_2CO_3 + Ca(OH)_2 = 2 KOH + CaCO_3$ .)
2. What per cent of Glauber's salt,  $Na_2SO_4 \cdot 10 H_2O$ , is sodium sulphate?
3. A gram of gunpowder produced 300 cc. of gas at 0° C. What would be the volume at 230° C.?
4. How much sodium will 2 kg. of sodium carbonate yield, if heated with carbon? (Assume  $Na_2CO_3 + C_s = Na_2 + 3 CO$ .)
5. What is the per cent of sodium in (a)  $NaOH$ , (b)  $Na_2SO_4$ , (c)  $NaCl$ , (d)  $HNaSO_4$ ?
6. What is the per cent of potassium in (a) potassium bromide ( $KBr$ ), (b) potassium nitrate ( $KNO_3$ ), (c) potassium iodide ( $KI$ )?

## CHAPTER XXII.

### COPPER—SILVER—GOLD.

**Introduction.**—These metals are related, but they do not form a group having such marked family characteristics as the alkali metals. The metals, as well as their alloys and compounds, have many domestic and commercial uses.

#### COPPER.

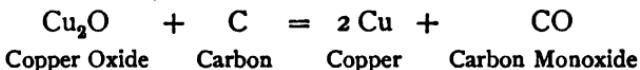
**Copper** has been known for ages. Domestic utensils and weapons of war containing copper were used before similar objects of iron. The Romans obtained copper from the island of Cyprus. They called it *cuprium aes* (*i.e.* Cyprian brass), which finally became simply *cuprum*. From *cuprum* we obtain the symbol Cu and the terms *cuprous* and *cupric*.

**Occurrence of Copper.**—Copper, both free and combined, is an abundant element. Single masses of native or metallic copper weighing many tons are found in Michigan mines on the shores of Lake Superior. The most valuable **ores** of copper are copper sulphide (chalcocite, copper glance,  $\text{Cu}_2\text{S}$ ), copper oxide (cuprite, ruby ore,  $\text{Cu}_2\text{O}$ ), the copper-iron sulphides (copper pyrites, chalcopyrite,  $\text{CuFeS}_2$ , and bornite,  $\text{Cu}_3\text{FeS}_3$ ), and the complex carbonates (malachite,  $\text{CuCO}_3\text{Cu}(\text{OH})_2$ , and azurite,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ).

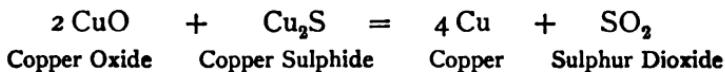
Native copper comes chiefly from Michigan (Fig. 71), the copper-iron sulphide ores from Montana, and the carbonates from Arizona.

The United States produced about 300,000 tons of copper in 1902, which was more than half of the world's supply. Of this amount Montana furnished about 38 per cent, Michigan 26 per cent, and Arizona 22 per cent. The annual output has steadily increased since 1896.

**Metallurgy of Copper.**—Copper is extracted from its ores by processes which vary with the composition of the ore. (1) Native copper ore is first crushed, then washed to remove impurities, and the concentrated product finally smelted and refined by a single fusion. (2) The carbonates and oxides are reduced by roasting them with coke in blast furnaces. The general chemical change may be represented thus—



(3) The smelting of copper-iron sulphides is complicated. The ore is crushed and washed, and then roasted in a furnace. This operation removes the adhering rock and changes much of the sulphide into an oxide. The roasted mass is then melted with coal and sand in a shaft or a reverberatory furnace, whereby the iron is largely changed into a fusible silicate, which runs off as a part of the slag. The remaining "matte," as it is called, contains from 50 to 65 per cent of copper, besides some iron, sulphur, and arsenic. It is roasted and melted until all the iron and arsenic are removed and mainly copper sulphide remains. This is finally roasted to convert it partly into an oxide, and the mixture of sulphide and oxide is again melted; the sulphur passes off as sulphur dioxide, and the copper is left behind. The equation for this final change is—



Sometimes the sulphur and arsenic are removed by forcing hot air through the molten sulphide.

**Purification of Copper.** — The crude copper from most ores contains about 98 per cent of copper. Such impure copper is best purified by electrolysis, and is called **electrolytic copper**. Thick plates of the impure copper are attached as anodes to the positive electrode of a powerful battery or dynamo and suspended in a solution of copper sulphate and sulphuric acid. Sheets of pure copper are attached as cathodes to the negative electrode and, of course, dip into the solution (Fig. 57). When the current passes, the crude copper anodes dissolve, pure copper is deposited upon the cathodes, and the impurities either remain in solution or fall to the bottom of the tank. In terms of the theory of electrolytic dissociation, copper ions ( $Cu^{++}$ ) migrate to the cathode, lose their charges, and become metallic copper.

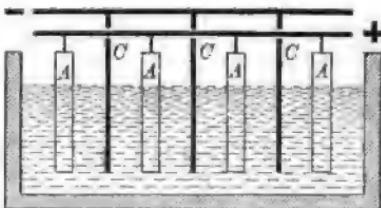


FIG. 57. — Apparatus for the preparation of pure copper by electrolysis. *A, A, A* are anodes, and *C, C, C* are cathodes.

**Properties of Copper.** — Copper is a bright metal, distinguishable from all others by its peculiar reddish color. It is flexible, hard, and tough; it can be drawn out into wire and rolled into very thin sheets. Its specific gravity is 8.9. Metallic copper is an excellent conductor of heat and electricity. Exposed to dry air, it turns dull, and in moist air it gradually becomes coated with a greenish copper carbonate. Heated in the air, it is changed into the black copper oxide, and at a high temperature it colors a flame emerald-green. With nitric acid it forms copper

nitrate and oxides of nitrogen (see Oxides of Nitrogen); with hot sulphuric acid it yields copper sulphate and sulphur dioxide (see Sulphur Dioxide). Hydrochloric acid has little effect upon it. Copper replaces some metals if suspended in solutions of their compounds, *e.g.* a clean copper wire soon becomes coated with mercury if placed in a solution of any mercury compound; on the other hand, metals like iron, zinc, and magnesium remove copper from its solution, *e.g.* a nail or knife blade soon becomes coated with copper if dipped into a solution of any copper compound. Scrap iron is often used to precipitate copper on a large scale.

**Test for Copper.**—(1) The reddish color, peculiar "coppery" taste, and green color given to a flame serve to identify metallic copper. (2) An excess of ammonium hydroxide added to the solution of a copper compound produces a beautiful blue solution. (3) A few drops of acetic acid and of potassium ferrocyanide solution added to a dilute solution of a copper compound produce a brown precipitate of copper ferrocyanide. These tests are characteristic and decisive.

**Uses of Copper.**—Next to iron, copper is the most useful metal. Enormous quantities of wire are used in operating the telegraph, cable, telephone, electric railway, and electric light. Sheet copper is made into household utensils, boilers, and stills. Copper bolts, nails, and rivets are used on ships, because the rust does not destroy wood as iron rust does. All nations use copper as the chief ingredient of small coins. Electrical apparatus utilizes much copper. Maps, etchings, and some kinds of engravings are printed from copper plates; calico is printed from a copper cylinder upon which the design is engraved. Books are printed and illustrated from an electrotype, made by depositing a film of copper upon an impression of the type or design in wax or plaster of Paris. In a similar way

many objects are copper plated (see Chapter X). Copper is an essential constituent of many alloys.

**Alloys of Copper** are important. **Brass** is a bright yellow alloy containing 63 to 72 per cent of copper, the remainder being zinc. It is made by melting these metals together. It can be drawn into wire, hammered into any shape, and turned in a lathe. It is harder than copper, and on account of its durability and elasticity has many uses for which copper is not suited. **Pinchbeck**, **Muntz metal**, **Bath metal**, **Dutch metal** (leaf or "gold"), are varieties of brass. **Muntz metal** is now used in place of sheet copper, as sheathing for the bottoms of ships, because it rusts very slowly. Typical **bronze** contains different proportions of copper, zinc, and tin. Some antique bronzes contain lead or iron. The per cent of copper is 70 to 95, of zinc 1 to 25, of tin 1 to 18. The proportions in the British bronze coinage are copper 95, zinc 1, tin 4. On account of its beautiful color and extreme durability, bronze is used for statues, memorial tablets, coins, and medals. The ancients made it into weapons of war and household utensils. Cannon were formerly made of bronze, but for this purpose steel is now used. **Phosphor bronze** contains a small per cent of phosphorus and of lead. It is tougher than ordinary bronze, and is used to make steamship propellers and parts of machines. **Silicon bronze** is copper with traces of iron and silicon, and is used for telegraph and telephone wires. **Aluminium bronze** contains 90 per cent copper and 10 per cent aluminium. It is a hard, yellow, elastic alloy, and is used in constructing hulls of yachts; its lightness, strength, and resistance to chemicals adapt it to many other uses.

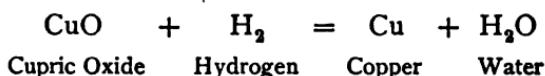
**Gun metal** is about 90 per cent copper and 10 per cent zinc; it was formerly used in making cannon, and is now used to some extent in

making firearms. Bell metal contains about 75 per cent copper and 25 per cent zinc. Speculum metal contains about 70 per cent copper, 30 per cent tin, and traces of zinc, nickel, and iron ; it takes a brilliant polish, and is used in optical instruments, especially telescopes, to reflect light. The different varieties of German silver contain different proportions of copper, nickel, and zinc. The per cent of copper is 50 to 60, of nickel 20 to 25, and of zinc about 20. In color and luster it resembles silver, for which it is often substituted. Its power to conduct electricity is only slightly affected by changes of temperature, hence it is often used in resistance coils. Chinese Pakfong (or paktong) is a variety of German silver. The nickel coins of Germany and the United States contain 75 per cent copper and 25 per cent nickel. Copper is also a constituent of many other coins. Britannia metal and white metal, in which copper is a minor constituent, are described under Alloys of Tin.

**Compounds of Copper.**—Copper forms two series of compounds, the cuprous and the cupric. Thus, there are cuprous oxide ( $Cu_2O$ ) and cupric oxide ( $CuO$ ), cuprous chloride ( $CuCl$ ) and cupric chloride ( $CuCl_2$ ). The cuprous compounds contain a larger proportion of copper than the cupric compounds. Not every member of each series is important, or even well known. Other metals—mercury and iron—form similar series. The most important compounds are the oxides and copper sulphate. Copper compounds are poisonous. Cooking utensils made of copper should be used with care. Vegetables, acid fruits, and preserves, if boiled in them, should be removed as soon as cooked. The vessels themselves should be kept bright, to prevent the formation of soluble copper salts, which might contaminate the contents.

**Cuprous Oxide**,  $Cu_2O$ , occurs native as cuprite or ruby ore. It may be obtained as reddish powder by heating a mixture of solutions of copper sulphate, Rochelle salt, sodium hydroxide, and grape sugar. This oxide colors glass ruby red. It is a beautiful mineral and a valuable ore.

**Cupric Oxide**, CuO, is a black solid formed by heating copper nitrate. It is reduced to metallic copper by hydrogen or by carbon, thus —



Hence it may be used to determine the gravimetric composition of water.

**Copper Sulphate**, CuSO<sub>4</sub>, is the most useful compound of copper. Like many of the cupric compounds it is a blue, crystallized solid, and is often called "blue vitriol" or "blue stone." The crystallized salt (CuSO<sub>4</sub>. 5 H<sub>2</sub>O) loses water in the air; heated to 240° C., all the water escapes, leaving a whitish powder. This **anhydrous copper sulphate** absorbs water from alcohol and similar liquids, and when added to water it again becomes blue. Copper sulphate is used in electric batteries, in making other copper salts, in calico printing, dyeing, copper plating, in preserving timber, and whenever a soluble copper compound is needed. It is poisonous and is one ingredient of certain mixtures which are sprayed upon trees to kill insects.

Copper sulphate may be prepared by treating copper with sulphuric acid. This method is used on a large scale, but some of the copper sulphate of commerce is a by-product obtained in refining gold and silver with sulphuric acid (see below).

**Copper Nitrate**, Cu(NO<sub>3</sub>)<sub>2</sub>, is a blue, crystallized solid, formed by the interaction of copper and dilute nitric acid. It is a cupric salt. It is very soluble in water, and is readily decomposed by heat into cupric oxide and oxides of nitrogen.

**Cuprous Sulphide**, Cu<sub>2</sub>S, is the bluish black mineral chalcocite. **Cupric sulphide**, CuS, is the black precipitate formed by passing hydrogen sulphide gas into a solution of a cupric salt.

**Malachite** is a bright green mineral and is often used as an ornamental stone. **Azurite** is a magnificent blue, crystallized mineral. Both are carbonates and valuable ores of copper.

#### SILVER.

**Silver** is one of the precious metals. From the remotest ages it has been used for ornaments, household vessels, and money.

The Latin name of silver is *argentum*, from which the symbol Ag is derived. The alchemists called it *luna*, on account of its silvery or "moonlike" appearance.

**Occurrence of Silver.** — Native silver is found in Arizona, Mexico, Norway; also in South America and Australia. The chief **ores** are the sulphides. The simple sulphide (silver glance, argentite,  $\text{Ag}_2\text{S}$ ) is the richest ore and is found in many localities in the United States. Silver sulphide is often combined with sulphides of lead, copper, antimony, or arsenic. These complex sulphides are found in Mexico, Peru, Bolivia, Chili, and in Idaho. Small quantities of native silver chloride (horn silver,  $\text{AgCl}$ ) are also found; it resembles wax or horn, and melts in a candle flame. Sea water contains traces of silver, the total quantity in the ocean being estimated to be about two million tons. Alloys of silver with gold, mercury, and copper are found; average California gold contains about 12 per cent silver. Many ores contain silver, especially those of lead; and this argentiferous (or silver-bearing) lead is one of the chief sources of silver.

The world's supply of silver comes mainly from the United States, Mexico, Germany, Australia, and Bolivia. The United States produced about sixty million ounces in 1908. This was about one third of the world's supply, and also the average annual output for the last few years. Of this vast quantity, about 90 per cent was furnished by Colorado, Montana, Utah, Idaho, California, and Nevada (Fig. 58).

**Metallurgy of Silver.** — Silver is extracted from its ores by two principal processes. (1) In the **amalgamation process** the powdered ore is first changed into silver

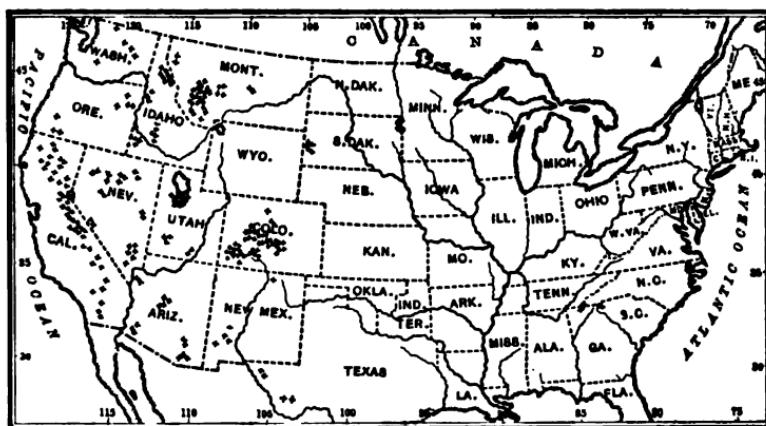
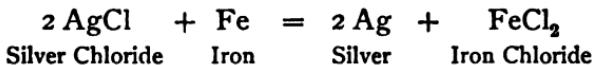


FIG. 58. — Distribution of silver and gold in the United States.

chloride by roasting (or simply mixing) it with sodium chloride. The mass is then reduced to silver by agitation with water and iron (or an iron compound); the simplest equation for this reaction is —



The silver is removed by adding mercury, which forms an amalgam (an alloy) with the silver, but not with the other substances. When the amalgam is heated, the mercury distils off, and the silver — with some gold — remains behind. (2) Silver is extracted from lead ores by the **Parkes process**. After the sulphur, arsenic, and other impurities have been removed from the lead ores, the final product is a mixture of lead, silver, and gold. This is melted and

thoroughly mixed with zinc. As the mixture cools, an alloy of silver, gold, zinc, and a little lead rises to the top, solidifies, and is removed. The remaining lead mixture is treated again with zinc. The alloy of silver, gold, zinc, and lead is heated to volatilize the zinc and to oxidize (or melt away) the lead. The mixture of silver and gold is heated with sulphuric acid; the gold is not acted upon, but the silver forms silver sulphate, which is reduced by copper to metallic silver (Fig. 59).



FIG. 59.—Bar or "brick" of silver showing the stamp of the United States Assay Office as a guarantee of its purity.

Lead ores containing considerable silver are sometimes subjected to **cupellation** to extract the silver. The ore or alloy is heated in a furnace having a shallow hearth made of porous, infusible bone ash. The lead is changed into an oxide (litharge), which melts, and is partly driven off by the air blast into pots and partly absorbed by the porous **cupel**. The silver is protected from the oxidizing power of the air by the melted litharge, but toward the end of the operation the thin film of litharge bursts, and the metallic silver appears as a bright disk if the operation is conducted in a furnace, and as a globule or button if the extraction is performed in a small assay cupel. The process is then stopped and the silver removed.

**Properties of Silver.** — Silver is a lustrous, white metal, which takes a brilliant polish. It is harder than gold, but softer than copper. Like copper, it is ductile and malleable, and may be easily made into various shapes. Its specific gravity is about 10.5, being heavier than copper,

but lighter than lead. It melts at about  $962^{\circ}$  C., and fuses readily on charcoal in the blowpipe flame; it vaporizes in the oxyhydrogen flame and in the electric furnace. Molten silver absorbs about twenty times its volume of oxygen, which is expelled violently when the silver solidifies. Like copper, silver is an excellent conductor of heat and electricity, but it is too costly for such uses. It does not tarnish in air, unless sulphur compounds are present, and then the familiar black film of silver sulphide is produced. This blackening is especially noticed on silver spoons which have been put into eggs or mustard, and on silver coins which have been carried in the pocket, the sulphur in the latter case coming from sulphur compounds in the perspiration; the tarnishing of household silver is due to sulphur compounds in illuminating gas or gas from burning coal. So-called "oxidized" silver is not oxidized, but coated with silver sulphide. Silver is only very slightly acted upon by hydrochloric acid, and not at all by molten caustic potash, soda, or potassium nitrate. Nitric acid and hot concentrated sulphuric acid change it into the nitrate and sulphate, respectively, as in the case of copper.

**Alloys of Silver.**—Pure silver is too soft for constant use, and is usually hardened by adding a small amount of copper. These alloys are used as coins and for jewelry. The silver coins of the United States and France contain 900 parts of silver to 100 of copper, and are called 900 fine. British silver coins are 925 fine; this quality is called "sterling silver," and from it much ornamental and useful silverware is made.

**Silver Plating.**—Metals cheaper than silver may be coated or plated with pure silver precisely as in the case of copper. Plated silverware has the appearance of solid or pure silver. The object to be plated is carefully cleaned,

and made the cathode in a bath or solution of potassium silver cyanide. The anode is a plate of pure silver (Fig. 60). The deposit of silver is dull, but may be brightened by rubbing with or without chalk.

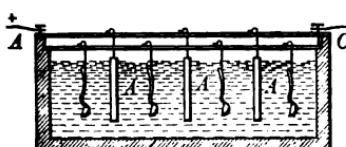


FIG. 60.—Apparatus for silver plating. *A, A, A*, are silver anodes, and the spoons are cathodes.

made by dissolving silver in nitric acid. Exposed to the light, it turns dark if in contact with organic matter. It discolors the skin; if applied long enough, it disintegrates the flesh, and is often used by physicians for this purpose. Its caustic action and the silvery color of the metal from which it is made long ago led to its name, **lunar caustic**. Besides its extensive use in photography and silver plating, silver nitrate is the essential constituent of indelible ink. **Silver chloride** ( $\text{AgCl}$ ) is made by adding hydrochloric acid or the solution of any chloride to a solution of a silver compound. Thus formed, it is a white, curdy solid, which turns violet in the light, and finally black. This action of light is more intense if organic matter is present. It dissolves in ammonium hydroxide, forming a complex compound of the two substances. The formation and properties of silver chloride constitute the **test for silver**. **Silver bromide** ( $\text{AgBr}$ ) and **silver iodide** ( $\text{AgI}$ ) are analogous to silver chloride in their properties and methods of formation. They are used in photography.

**Photography** is based on the fact that silver salts, especially the bromide and iodide, change color when mixed with organic matter and exposed to the light. The photograph is taken on a glass **plate**, coated on one side with a

### Compounds of Silver.—

The most important compound is **silver nitrate** ( $\text{AgNO}_3$ ).

It is a white crystalline solid,

thin layer of gelatine, containing the silver salts. Sometimes a sheet of sensitized gelatine, called a **film**, is used. The plate or film is placed in the camera and **exposed**. The light, which comes from the object being photographed, changes the silver salts in proportion to its brilliancy. The plate, however, shows no change until it has been **developed**. This process consists in treating the plate with a reducing agent, *e.g.* ferrous sulphate, pyrogallic acid, or special mixtures. As the **developer** acts upon the plate, the image appears. This is really a deposit of finely divided silver. Where the intense light fell upon the plate, the deposit is heavier than where little or no light fell. Hence, dark parts of the object appear light on the plate, and light parts dark; and since the image is the reverse of the object, the plate is called a **negative**. When the plate has been properly developed, it still contains silver salts not altered by the light; and if they were left on the plate, the image would be clouded, and finally obliterated by the light. The image is, therefore, **fixed** by washing off the silver salts with a solution of sodium thiosulphate (or "hyposulphite"). A **print** is made by laying sensitized paper upon the negative and exposing them to the sunlight, so that the light will pass through the negative. The negative obstructs the light in proportion to the thickness of the silver deposit, so the photograph has the same shading as the object. Most prints, like the plates, must be fixed. Sometimes the color is improved by **toning**, *i.e.* by placing the print in a solution of gold or of platinum.

#### GOLD.

**Gold** is the most precious of the metals, and has been used from the earliest times for adornment and as money.

The Latin name of gold, *aurum*, gives the symbol Au. For many centuries the alchemists tried to produce gold from base or cheaper metals. They were unsuccessful in their search for the Philosopher's Stone, which they believed had power to effect this transformation.

**Occurrence of Gold.**—Gold is widely distributed, but not abundantly in many places. Unlike copper and silver, its compounds are few and rare; the only important ones are the tellurides (compounds of tellurium) found in Colorado. It is never found pure, being alloyed with silver and occasionally with copper or iron. It is disseminated in fine, almost invisible, particles among ores of other metals, though not so abundantly as silver. Much gold is found in veins of quartz, and in the sand and gravel formed from gold-bearing rocks. Gold occurs usually as dust, scales, or grains, but occasionally shapeless masses called "nuggets" are found, varying in weight from a few grams to many kilograms. The largest nugget ever known weighed over 84 kg. (184 lbs.).

The chief **gold-producing countries** are the United States, Australia, South Africa, and Russia. The United States produces annually over four million ounces, which come largely from Colorado, California, and other Western states, and Alaska. Gold in working quantities is found in about twenty states of the Union (Fig. 58). The total value of the gold produced in the world annually is about \$400,000,000.

**Gold Mining.**—Gold was first obtained by miners by washing the gold-bearing sand and gravel of a stream in large pans or cradles. This primitive method was soon replaced by **placer mining** and **hydraulic mining**. Streams of water, directed against the earth containing the gold, wash away the lighter materials, but leave the heavy gold behind in the form of scales or "gold dust." From this mixture gold and silver are extracted by mixing with mercury, or by passing the moistened mass over copper plates

coated with mercury. The amalgam is then heated, as in the metallurgy of silver, to remove the mercury; the residue of gold and silver is purified as described below. In **vein mining** the gold-bearing rock — usually quartz — is crushed and then washed, and the gold removed by mercury, as in placer mining (see Chapter XX). Low grade ores and those containing certain metals cannot be profitably treated with mercury. In the **chlorination process** the crushed ore is roasted and then revolved in barrels containing bleaching powder and sulphuric acid; this operation forms a soluble gold chloride ( $\text{AuCl}_3$ ), from which the gold is precipitated as a fine powder by hydrogen sulphide (or other reducing agents). In the **cyanide process** the crushed ore, or the slime from a previous extraction, is mixed with a weak solution of potassium cyanide and exposed to the air; this operation changes the gold into a soluble cyanide ( $\text{KAu}(\text{CN})_2$ ). The gold is separated from this solution by **electrolysis** or by treatment with zinc.

**Purification of Gold.** — Gold obtained by the above methods is impure, silver being the chief impurity. These metals are **parted** by a chemical process or separated by **electrolysis**. By the old parting process known as **quar-tation** an alloy of gold and silver, in which the gold is about one fourth of the whole, is treated with nitric acid; this operation changes the silver into the nitrate from which the pure gold may be readily removed. The metals may be parted by the cheaper method described under silver, viz. by boiling with concentrated sulphuric acid. By this treatment the gold, which is about one sixth of the alloy, is left as a brownish, porous mass. It is washed, dried, and fused with charcoal and sodium carbonate. In one **electrolytic method** of separation, the anode is an alloy of gold and silver, the cathode is silver, and the elec-

trolyte is silver nitrate. When the current passes, part of the silver of the anode goes into solution as the nitrate, while part is deposited at the cathode; the gold remains at the anode as a fine powder and is caught in a cloth bag which incloses the whole anode. Gold is now purified at the United States Mints by electrolysis. The electrolyte is a solution of gold chloride, the anode is an alloy rich in gold, and the cathode is pure gold. Gold is deposited on the cathode, and silver chloride around the anode.

The purity of gold is expressed in **carats**. Pure gold is 24 carats fine; an alloy containing 22 parts of gold and 2 parts copper is 22 carat gold, while one containing equal parts gold and other metals is 12 carat gold (see foot-note, page 183).

**Properties of Gold.**—Gold is a yellow metal. It is about as soft as lead, and is the most ductile and malleable of all metals. The leaf into which it may be beaten is very thin and is green by transmitted light. Air, oxygen, and most acids do not attack it; but it is changed into a gold chloride ( $\text{AuCl}_3$ ) by *aqua regia* (see *Aqua Regia*). Gold is one of the heaviest metals, its specific gravity being about 19.

**Uses of Gold.**—Pure gold is too soft for most practical purposes, and is, therefore, usually hardened with copper or silver. The gold-copper alloy has a reddish color and is often called "red gold"; the gold-silver alloy is paler than pure gold and is sometimes called "white gold." Gold coins contain gold and copper. The United States standard gold coins contain 9 parts gold and 1 part copper, while in England the legal standard is 11 of gold to 1 of copper. Gold leaf of various grades is used to ornament books, signs, and many objects. Jewelers use gold for many purposes; such gold varies from 12 to 22 carats.

in purity. On account of its malleability, feeble chemical action, and beauty, gold is used by dentists for filling teeth.

**Compounds of Gold** are readily decomposed by metals, weak reducing agents (*e.g.* ferrous sulphate or hydrogen sulphide), fine solids like charcoal, and by electrolysis. When gold is dissolved in *aqua regia* and the acid removed by evaporation, the resulting gold chloride ( $\text{AuCl}_3$ ) gives with stannous chloride solution a beautiful purple precipitate; the latter is called "purple of Cassius," and is probably finely divided gold. Its formation is the test for gold. The process of gold plating is the same as silver plating, only the solution is one of potassium gold cyanide ( $\text{Au}(\text{CN})_3 \cdot \text{KCN}$ ) and the anode is gold. Much cheap jewelry is gold plated.

#### EXERCISES.

1. What is the symbol of (*a*) copper, (*b*) silver, (*c*) gold? State the derivation of each symbol.
2. Where is copper found abundantly? State in what form it occurs in each locality. Discuss its production.
3. Describe briefly the metallurgy of (*a*) native copper, (*b*) oxides and carbonates, (*c*) copper-iron sulphides.
4. Describe the purification of copper by electrolysis.
5. State (*a*) the physical properties of copper, and (*b*) the chemical properties.
6. Describe several tests for copper.
7. Discuss the uses of copper.
8. Name ten alloys of copper. Describe five important alloys.
9. What is an electrotype? How is it made? (See Chapter X.)
10. State the general properties of copper compounds.
11. Describe the oxides of copper.
12. Describe the manufacture, and state the properties and uses of copper sulphate.
13. What are the properties of (*a*) copper nitrate, (*b*) malachite, and (*c*) azurite?
14. What is the formula of (*a*) copper sulphate, (*b*) copper nitrate, (*c*) cupric oxide, and (*d*) cuprous oxide?
15. Discuss (*a*) the occurrence, and (*b*) the production of silver.
16. Describe the extraction of silver by (*a*) the amalgamation process, and (*b*) the Parkes process.

17. State (a) the physical properties of silver, and (b) the chemical properties.
18. Discuss (a) silver alloys, and (b) silver plating.
19. State the properties and uses of silver nitrate.
20. State the properties of silver chloride. What is the test for silver?
21. Describe briefly the essential operations in photography. What general chemical changes does it utilize?
22. What is (a) blue vitriol, (b) argentiferous lead, (c) oxidized silver, (d) sterling silver, (e) coin silver, (f) lunar caustic, and (g) "hypo"?
23. What is the formula of (a) silver nitrate, and (b) silver chloride?
24. Discuss (a) the occurrence of gold, and (b) its production.
25. Describe the different methods of (a) mining, and (b) extracting gold.
26. Describe the purification of gold by (a) parting, and (b) electrolysis.
27. What is 18 carat gold?
28. State (a) the properties, and (b) the uses of gold.
29. Discuss (a) compounds of gold, and (b) gold plating.
30. What is the test for gold?
31. What is (a) gold dust, (b) *aqua regia*, (c) a nugget, (d) gold leaf?

#### PROBLEMS.

1. How much cupric oxide is formed by heating 1467 gm. of copper in air? (Assume  $\text{Cu} + \text{O} = \text{CuO}$ .)
2. Calculate the per cent of copper in (a) malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ), (b) azurite ( $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ), (c) copper sulphate ( $\text{CuSO}_4$ ).
3. If 480 gm. of silver interact with nitric acid, how much silver nitrate is formed?
4. Calculate the per cent of silver in (a) silver chloride ( $\text{AgCl}$ ), (b) silver sulphide ( $\text{AgS}_2$ ), (c) silver nitrate ( $\text{AgNO}_3$ ).

## CHAPTER XXIII.

### CALCIUM, STRONTIUM, AND BARIUM.

THESE elements form a natural group called the **alkaline earth metals**. The metals themselves are rare, but their compounds, especially those of calcium, are numerous and useful. This group resembles the alkali group.

#### CALCIUM.

**Occurrence of Calcium.**—Calcium is never found free. Combined calcium makes up about 3.5 per cent of the earth's crust. The most abundant compound is calcium carbonate ( $\text{CaCO}_3$ ). This has many familiar forms, *e.g.* limestone, chalk, marble, coral, and shells. Many rocks are complex silicates of calcium and other metals. The extensive deposits of calcium phosphate, calcium borate, and calcium fluoride have been mentioned. Calcium sulphate ( $\text{CaSO}_4$ ) occurs abundantly in the form of gypsum, alabaster, and selenite. Calcium compounds are essential to the life of plants and animals, being found in the leaves of plants, and in the bones, teeth, and shells of animals. Many rivers and springs contain calcium salts, especially the acid carbonate and sulphate.

**Preparation and Properties.**—Metallic calcium was obtained by electrolysis in 1808 by Davy, but our knowledge of the pure metal is due to Moissan. In 1898 he prepared it from the iodide by electrolysis. It is now prepared by the electrolysis of fused calcium chloride. The anode is a graphite crucible and the cathode is a rod of iron which can be elevated by a screw.

Calcium is a silver-white metal, soft enough to be cut with a file, though much harder than lead. It may be crystallized from melted sodium. It readily decomposes water at the ordinary temperature, and combines directly with most of the other elements.

**Calcium Carbonate,  $\text{CaCO}_3$ .**—The most abundant form of this compound is **limestone**. Vast deposits are found in many places, exhibiting a variety of textures and colors. In the United States much limestone is found in Iowa, Illinois, and Wisconsin. All kinds are compact and usually soft, though some are hard enough for use as building stone; some are coarse, and often consist of grains, crystals, or small shells. Pure limestone is white or gray, but

impurities, especially organic matter and iron compounds, produce blue, yellow, reddish, and black varieties. Hard, crystalline limestone which takes a good polish is called **marble**. This form, which has a wide range of color, is used as a building and an ornamental stone. **Calcite**

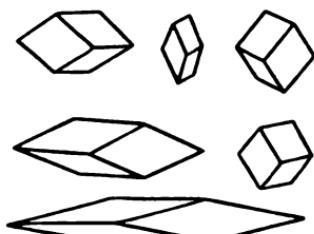


FIG. 61.—Calcite crystals.

is crystallized calcium carbonate. It is almost as abundant as quartz, though softer; its varied color and crystal form combine to make it attractive (Fig. 61). A very transparent variety of calcite called **Iceland spar** has the remarkable property of double refraction, *i.e.* of making objects appear double (Fig. 62).



FIG. 62.—Crystallized Iceland spar showing double refraction.

Calcium carbonate is not soluble in water, unless carbon dioxide is present (see Carbon Dioxide). As water containing carbon dioxide works its way underground in limestone regions the limestone is dissolved and caves



FIG. 63.—Stalactites and stalagmites in Luray Cavern.  
From a photograph copyrighted by C. H. James.

are often formed or enlarged. When the water enters a cave and drips from the top, the water evaporates, or the gas escapes, or both, and the calcium carbonate is redeposited, often forming **stalactites** and **stalagmites** (Fig. 63). The stalactites hang from the roof like icicles,

while the stalagmites grow up from the floor, as the deposit slowly accumulates from the solution which drops from the roof or the tips of stalactites. The Mammoth Cave in Kentucky, the Marengo Cave in Indiana, and the Luray Cavern in Virginia are famous for these fantastic formations. **Mexican onyx** is a variety of stalagmite. Vast deposits of this beautiful mineral are found in Algeria and Mexico. It is translucent and delicately colored, and is used as an ornamental stone, especially for altars, table tops, mantels, and lamp standards. Beautiful deposits of limestone are found around many mineral springs. **Travertine** occurs near many springs in Italy. When fresh, it is soft and porous, but it soon hardens and becomes a durable building stone in dry climates. The outer walls of the Colosseum and of St. Peter's are travertine. Limestone often contains shells and fossils, confirming our belief that limestone is the remains largely of the shells of animals. The calcium carbonate dissolved in the ocean is transformed by marine organisms into shells and bony skeletons. The hard parts of these animals accumulate in vast quantities on the ocean bottom, become compact, often hardened and crystallized, and are finally elevated into their present position. On the coast of Florida, **coquina** or shell rock is found. It is a mass of fragments of shells cemented by calcium carbonate, and in time will become compact limestone. **Chalk** is the remains of shells of minute animals. When examined under a microscope, a good specimen is seen to consist almost entirely of tiny shells. The ocean contains myriads of minute animals, and when they die, their shells, which are calcium carbonate, sink to the bottom. As a result, the ocean bottom is partly covered with a gray mud, called globigerina ooze. Under the microscope this

ooze looks like Figure 64, and when dried and compressed it can hardly be distinguished from chalk. Hence it is believed that the immense beds of chalk found in England and other places were formed from this ooze. Some varieties of chalk under the microscope resemble the ooze



FIG. 64.—Ooze from the ocean bottom, showing globigerina shells (magnified).

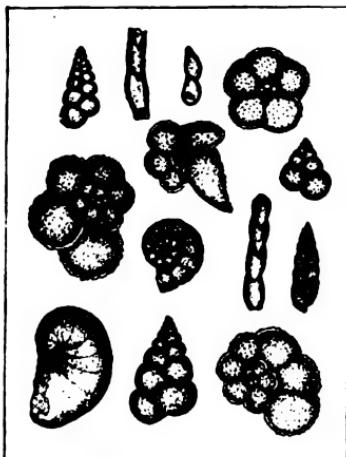


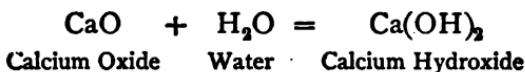
FIG. 65.—Chalk from Iowa, showing globigerina shells (magnified).

(Fig. 65). **Blackboard crayon** is a mixture of chalk and clay. **Whiting** is a variety of impure chalk; **putty** is a mixture of whiting and oil. **Coral** is calcium carbonate. The vast accumulations in the sea are the skeletons of the coral animals.

The properties of calcium carbonate, discussed in Chapter XIV, may be profitably reviewed at this point.

Besides being burned into lime, immense quantities of limestone are consumed in manufacturing iron and steel, the United States alone using annually over seven million tons in this industry.

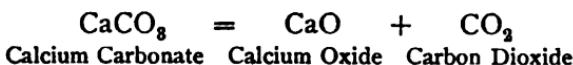
**Calcium Oxide**, CaO, is the chemical name of lime. It is a hard, white solid. Pure lime is almost infusible, and when heated in the oxyhydrogen flame, it gives an intensely bright light, sometimes called the "lime light" (see Hydrogen). In the electric furnace it melts and volatilizes, if the heating is prolonged. Lime containing impurities, like sand, clay, and iron compounds, melts quite readily into a glass or slag. Exposed to the air, lime becomes "air slaked," *i.e.* it slowly absorbs water and carbon dioxide, swells, and soon crumbles to a powder, which is a mixture of calcium hydroxide and calcium carbonate. Lime and water combine violently and liberate considerable heat, as is often seen when mortar is being prepared. This operation is called "slaking," and the product is "slaked lime." The equation for the chemical change is—



Fresh lime attacks organic matter, and is therefore often called "caustic lime" or **quicklime**. It combines with water to form calcium hydroxide and with acids to form calcium salts.

Lime is one of the most important substances. It is used in preparing mortar, cement, metals, in making bleaching powder, calcium carbide, sodium hydroxide, and glass, in purifying illuminating gas and sugar, to remove hair from hides before the process of tanning, in dyeing and bleaching cotton cloth, in drying gases, and as a disinfectant and fertilizer.

Lime is prepared on a large scale by heating limestone in a partly closed cavity or vessel. The decomposition takes place according to the equation —



The carbon dioxide gas escapes and the lime is left in the kiln.

Limestone was formerly "burned" in a cavity on a hillside, and in some regions it is so prepared to-day. An arch of limestone is built across the cavity above the fire pit, and limestone is introduced until the kiln is full. These kilns are being replaced by a modern kiln (Fig. 66), constructed so that the heat can be regulated (at *B*, *B*), the gases swept out, and the product removed continuously (at *C*, *C*).

Limestone, containing more than 10 per cent of clay, forms **hydraulic lime**, which becomes very hard when wet or kept in contact with water. **Cements** are varieties of hydraulic lime. They are made by burning a mixture (natural or artificial) of limestone, clay, and sand, and grinding the product to a very fine powder. Rosendale and Portland are the common brands.

**Calcium Hydroxide**,  $\text{Ca}(\text{OH})_2$ , is a white powder. It is sparingly soluble in water, but more soluble in cold than in warm water. The solution has a bitter taste, an alkaline reaction, and is commonly called **limewater**. Exposed to the air, limewater becomes covered with a thin crust of calcium carbonate, owing to the absorption of carbon dioxide. For the same reason, limewater becomes milky or cloudy when carbon dioxide is passed into it. The formation of calcium carbonate in this way is the usual **test for carbon dioxide**. The equation for this chemical change is —

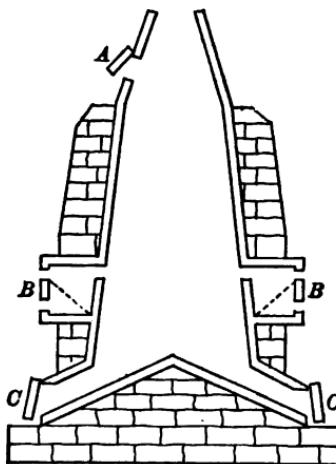
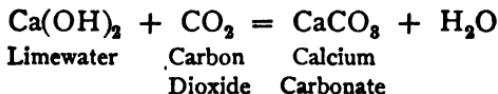


FIG. 66. — Continuous limekiln.

Limewater is prepared by carefully adding lime to considerable water, allowing the mixture to stand until the solid has settled, and then removing the pure liquid. When considerable calcium hydroxide is suspended in the liquid, the mixture is called **milk of lime**. Ordinary **whitewash** is thin milk of lime. Limewater is used in the chemical laboratory and as a medicine.

**Mortar** is a thick paste formed by mixing lime, sand, and water. It slowly hardens or "sets," owing to the loss of water and to the absorption of carbon dioxide. It hardens without much shrinking, and when placed between bricks or stones holds them firmly in place. The sand makes the mass porous and thus facilitates the change of the hydroxide into the carbonate. The sand itself is changed chemically only to a slight extent, if at all. Hair is sometimes added to make the mortar stick better, especially when it is used as **plaster** for walls.

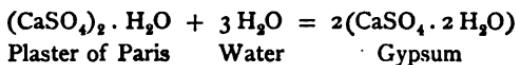
**Calcium Sulphate**,  $\text{CaSO}_4$ .—Extensive deposits of the different forms of calcium sulphate are found in England, France, Nova Scotia, and in the United States, especially in Michigan, Kansas, Iowa, Virginia, Tennessee, and Kentucky. It is generally found in volcanic regions, and is often associated with sulphur and limestone, one variety (**anhydrite**,  $\text{CaSO}_4$ ) being found with salt. **Gypsum** occurs as white masses or transparent crystals, having the composition  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ . Lustrous, translucent, soft crystals are called **selenite**. Fine grained, massive kinds are known as **alabaster**, and the fibrous kinds as **satin spar**.

Gypsum is widely used as a fertilizer, and in making glass and porcelain. Alabaster, being soft and beautiful, is carved into statues and other ornaments.

Calcium sulphate, when heated, loses its water of crystallization, becomes opaque, and falls to a powder. This powder, if moistened, swells and quickly "sets" or solidifies.

fies to a white, porous mass with a smooth surface. When properly prepared this powder is **plaster of Paris**, which derives its name from the celebrated gypsum beds near Paris. Plaster of Paris is used to coat walls, to cement glass to metal, but more largely to make casts and reproductions of statues and small objects. **Stucco** is essentially a mixture of glue and plaster of Paris.

To make plaster of Paris, lumps of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) are heated to about  $125^\circ\text{ C}.$  to expel part of the water. The product ( $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ ) is ground fine. The "setting" is a chemical change. The slightly soluble plaster of Paris slowly combines with water to form a network of very small crystals of the less soluble hydrated calcium sulphate. The equation is —



**Calcium Compounds and Hardness of Water.**—Calcium sulphate is slightly soluble in water, and calcium carbonate, as we have already seen, is changed into the unstable acid carbonate by water containing carbon dioxide. Water containing these salts of calcium is called **hard water**. They form sticky, insoluble compounds with soap, and as long as water contains such salts, the soap is useless as a cleansing agent. Heat decomposes acid calcium carbonate, and the hardness due to calcium carbonate is called **temporary hardness**, because boiling removes it. But the hardness caused by calcium sulphate cannot be so removed, and is called **permanent hardness**. Magnesium sulphate, like calcium sulphate, produces permanent hardness. **Soft water**, such as rain water, contains little or no calcium or magnesium salts.

**Calcium Chloride**,  $\text{CaCl}_2$ , is a white solid. It absorbs moisture rapidly, and is used to dry many gases and liquids. The crystallized variety dissolves readily in

water, and the solution is attended by a marked fall of temperature. A mixture of crystallized calcium chloride and snow produces a temperature of  $-40^{\circ}$  C. The liquid left from the interaction of calcium carbonate and hydrochloric acid contains calcium chloride, which on concentration is deposited in large crystals. These readily absorb water, but lose their own water of crystallization when heated above  $200^{\circ}$  C. This anhydrous calcium chloride is porous, and is the form usually used as a drying agent. At a high temperature it melts, and solidifies in cooling to a hard mass known as fused calcium chloride.

Calcium chloride is found in small quantities in some of the Stassfurt salts. It is obtained in large quantities as a by-product in the manufacture of sodium carbonate (by the Solvay process) and other chemicals.

**Other Compounds of Calcium** have already been discussed and may be reviewed here. They are calcium fluoride, calcium carbide, the calcium phosphates, and calcium hypochlorite. **Calcium sulphide** ( $\text{CaS}$ ) is formed by heating a mixture of gypsum and carbon; like other sulphides, it stains silver brown.

**Test for Calcium.** — Calcium compounds, especially the chloride, color the Bunsen flame a yellowish red.

#### STRONTIUM AND BARIUM.

**Strontium**, Sr, and **Barium**, Ba, are uncommon metallic elements. They resemble calcium closely in their physical properties and chemical relations. The metals themselves never occur free, and are hardly more than chemical curiosities. Their compounds are abundant, and some are useful.

**Compounds of Strontium.** — The important native compounds are the beautifully crystallized minerals, **strontianite** (strontium carbonate,  $\text{SrCO}_3$ ) and **celestite** (strontium sulphate,  $\text{SrSO}_4$ ). **Strontium oxide** (strontia,  $\text{SrO}$ ), like lime, is made by heating the carbonate. It unites with water to form **strontium hydroxide** ( $\text{Sr(OH)}_2$ ), which is used in the manufacture of beet sugar. **Strontium nitrate** ( $\text{Sr(NO}_3)_2$ ) and other salts of strontium color a flame crimson, and are widely used in

making fireworks, especially "red fire." The latter is a mixture of potassium chlorate, shellac, and strontium nitrate.

The production of the crimson colored flame is the test for strontium.

**Compounds of Barium.**—The most abundant native compounds are **witherite** (barium carbonate,  $\text{BaCO}_3$ ) and **barite** (barium sulphate,  $\text{BaSO}_4$ ). The **oxides**,  $\text{BaO}$  and  $\text{BaO}_2$ , have already been mentioned as a source of oxygen. **Barium hydroxide** ( $\text{Ba(OH)}_2$ ) solution is often called **baryta water**, and it forms the insoluble barium carbonate ( $\text{BaCO}_3$ ) when exposed to carbon dioxide. **Barium chloride** ( $\text{BaCl}_2$ ) is used in the laboratory to test for sulphuric acid and soluble sulphates, because it readily interacts with them and forms the insoluble **barium sulphate** ( $\text{BaSO}_4$ ). This precipitated salt is a fine, white powder, and being cheap and heavy it is a common adulterant of the ordinary white paint. Ground native barium sulphate has a similar use. Barium sulphate is also used to increase the weight of paper and to give it a gloss. Barium salts color a flame green, and **barium nitrate** ( $\text{Ba(NO}_3)_2$ ) is extensively used in making fireworks, especially "green fire." Commercial **barium sulphide** ( $\text{BaS}$ ), as well as the sulphides of calcium and strontium, shine feebly in the dark, after having been exposed to a bright light. On account of this property they are used in making **luminous paint**. Soluble barium salts are poisonous.

The production of the green flame is the test for barium.

#### EXERCISES.

1. Name the alkaline earth metals. What is the symbol of each?
2. Name several compounds of calcium. What proportion of the earth's crust is calcium?
3. Describe the preparation and state the properties of calcium.
4. What is the formula of calcium carbonate? State the properties, occurrence, and uses of (a) limestone, and (b) marble.
5. State the essential characteristics of (a) calcite, (b) Iceland spar, (c) stalactites, (d) Mexican onyx, (e) travertine, (f) coquina, (g) chalk, (h) coral.
6. Review the properties of calcium carbonate, especially its solubility (see Chapter XIV).
7. State the uses of (a) limestone, (b) marble, (c) chalk.
8. Describe the formation of (a) limestone caves, (b) chalk, (c) coral.

9. What is the formula and chemical name of lime? State the properties and uses of lime. How is it made? State the equation for the chemical change.
10. What is (a) quicklime, (b) slaked lime, (c) hydraulic lime, (d) Portland cement, (e) "air-slaked" lime?
11. What is the formula of calcium hydroxide? How is it formed? What are its properties? How does it interact with carbon dioxide? State the equation for the reaction.
12. What is (a) limewater, (b) milk of lime, (c) whitewash?
13. What is mortar? How is it prepared? For what is it used? How does it change chemically with age? What is plaster?
14. Discuss the occurrence of calcium sulphate. State the chief properties of (a) gypsum, (b) selenite, (c) alabaster, (d) satin spar. For what are gypsum and alabaster used?
15. What is plaster of Paris? Why so called? How is it prepared? What is its chief property? What are its uses? What is the chemical explanation of "setting"? What is stucco?
16. What is hard water? How does it act with soap? What is (a) temporary hardness, and (b) permanent hardness? How may each be removed? What is soft water? Why is rain water often called soft water?
17. Summarize the properties of calcium chloride. What is its formula? How is it prepared?
18. Review the essential properties of (a) calcium fluoride, (b) calcium carbide, (c) tricalcium phosphate, (d) bleaching powder.
19. What is the test for (a) calcium, (b) strontium, (c) barium?
20. State the use of (a) strontium hydroxide, and (b) strontium nitrate.
21. For what are (a) barium hydroxide, (b) barium nitrate, (c) barium sulphide, and (d) barium chloride used? Describe barium sulphate.

#### PROBLEMS.

1. What is the per cent of calcium in (a) marble ( $\text{CaCO}_3$ ), (b) gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ), (c) fluor spar ( $\text{CaF}_2$ ), (d) superphosphate of lime ( $\text{CaH}_4(\text{PO}_4)_2$ )?
2. How many tons of limestone must be heated to produce 100 tons of quicklime? (Assume  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ .)
3. Calculate the simplest formula of a compound having the percentage composition Ca = 40, C = 12, O = 48.

## CHAPTER XXIV.

### MAGNESIUM, ZINC, CADMIUM, AND MERCURY.

THESE elements form a natural group, though the members are not so closely related as the alkali and alkaline earth groups. Zinc and cadmium are much alike, and both also resemble magnesium. Mercury differs somewhat from zinc and cadmium, but resembles copper.

#### MAGNESIUM.

**Occurrence of Magnesium.** — Magnesium is never found free. In combination it is widely distributed and very abundant, constituting about 2.5 per cent of the earth's crust. Dolomite is magnesium calcium carbonate ( $\text{CaMg}(\text{CO}_3)_2$ ); it forms whole mountain ranges and vast deposits; beds hundreds of feet thick cover thousands of square miles in the upper Mississippi valley. Dolomite closely resembles marble and limestone. Magnesium carbonate is also abundant. Many of the Stassfurt salts contain magnesium, for example, kainite ( $\text{KCl}, \text{MgSO}_4 \cdot 3 \text{H}_2\text{O}$ ), carnallite ( $\text{KCl}, \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ ), and kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ). It is also a component of serpentine, talc, soapstone, asbestos, meerschaum, and other silicates. The sulphate and chloride are found in sea water and in mineral springs.

Through the decay of rocks, magnesium compounds find their way into the soil, from which they are taken up by plants. **Magnesium phosphates** are found in the bones of animals and the seeds of grains, and also in guano.

**Preparation of Magnesium.**—Magnesium was formerly prepared by reducing the chloride with sodium. It is now economically manufactured by **electrolysis**. A sketch of the essential parts of the apparatus is shown in Figure 67. Carnallite is put into the cylindrical iron vessel, *C*, which is the cathode. This is closed by the air-tight cover through which pass the pipes, *D*, *D'*, for conveying inert gases into and out of the apparatus. The carbon anode, *A*, dips into the carnallite and is inclosed by the porcelain cylinder, *B*, which is provided with a pipe, *E*, for the escape of the chlorine liberated at the anode.

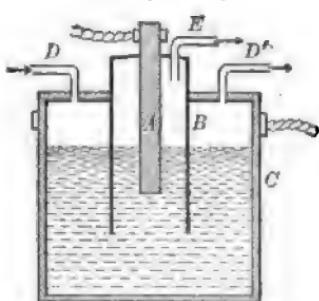


FIG. 67.—Apparatus for the manufacture of magnesium by the electrolysis of carnallite.

The carnallite is kept fused by external heat. When the current passes, the chlorine liberated at the anode escapes through *E*, and the magnesium liberated at the cathode floats on the fused carnallite and is prevented from oxidizing by the inert gas supplied through *D*. The porcelain cylinder, *B*, prevents the chlorine from escaping into the larger vessel. The molten magnesium is carefully removed at intervals.

**Properties of Magnesium.**—Magnesium is a lustrous, silvery white metal. It is a light metal, the specific gravity being only 1.75. It is tenacious and ductile, and when hot may be drawn into wire or pressed into ribbon, the latter being a common commercial form. It melts at a red heat and may be cast into different shapes. At a high temperature it volatilizes. It is easily kindled by a match or candle, and burns with a dazzling white light, producing dense white clouds of magnesium oxide ( $MgO$ ). It does not tarnish in dry air, but in moist air it is soon covered with a film of oxide. It liberates hydrogen from acids. Heated in nitrogen, it forms magnesium nitride ( $Mg_3N_2$ ; see Composition of Ammonia).

**Uses of Magnesium.**—Magnesium in the form of powder is used chiefly in taking flash-light photographs.

Small quantities are used in making fire-works; and both the powder and wire are used in the chemical laboratory.

**Magnesium Oxide**,  $\text{MgO}$ , is a white, bulky powder. It is formed when magnesium burns in the air, but it is manufactured by gently heating magnesium carbonate, just as lime is made from limestone. It is often called **magnesia**, or calcined magnesia. The native oxide is the mineral periclase. Magnesia dissolves with difficulty in water, forming **magnesium hydroxide** ( $\text{Mg(OH)}_2$ ). A mixture of magnesia and water, with or without magnesium chloride, hardens on exposure to the air, and is often used as a cement or artificial stone. Native magnesium hydroxide is the mineral brucite. Like lime, magnesia withstands a high temperature, and is, therefore, used as the chief ingredient of a protective mixture for steam pipes and vessels which are subjected to great heat. Magnesia is used as a medicine for dyspepsia and an antidote for poisoning by mineral acids.

**Magnesium Sulphate**,  $\text{MgSO}_4$ , is a white solid. There are several crystallized varieties. The native salt kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) when added to water changes into **Epsom salts** ( $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ ). This variety was first found in the mineral spring at Epsom, England. It is very soluble in water, and its solution has a bitter taste. It is extensively used as a medicine, in manufacturing sulphates of sodium and potassium, as a fertilizer in place of gypsum, and as a coating for cotton cloth.

**Magnesium Chloride**,  $\text{MgCl}_2$ , is a white solid. It is a by-product in the preparation of potassium chloride. The crystallized salt ( $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ ) is very deliquescent. Magnesia mixture is a mixture of magnesium chloride, ammonium chloride, and ammonium hydroxide; it is used in chemical analysis.

**Magnesium Carbonate**,  $MgCO_3$ , occurs native as **magnesite**, and combined with calcium carbonate as **dolomite**. The commercial salt known as **magnesia alba**, or simply **magnesia**, is a complex compound ( $Mg(OH)_2 \cdot 4 MgCO_3 \cdot 4 H_2O$ ). Several of these complex basic carbonates are known. Many face powders consist chiefly of **magnesia alba**.

It was during an investigation of **magnesia alba** that Black discovered carbon dioxide and showed the close relation between analogous compounds of magnesium and calcium.

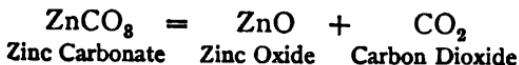
**Miscellaneous.** — Besides the oxide and sulphate, other compounds are used as medicines. **Fluid magnesia**, prepared by dissolving magnesium carbonate in water containing carbon dioxide, is a mild laxative. **Magnesium citrate** has a similar action; it is an effervescent mixture prepared from sodium bicarbonate, tartaric and citric acids, sugar, and magnesium sulphate.

#### ZINC.

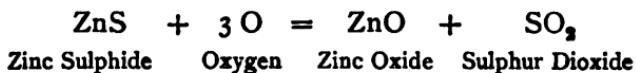
**Occurrence of Zinc.** — Free zinc is never found. The ores of zinc are not numerous, but are widely distributed. The chief ores are zinc sulphide (sphalerite, zinc blende,  $ZnS$ ), zinc carbonate (smithsonite,  $ZnCO_3$ ), zinc silicate (calamine,  $H_2Zn_2SiO_5$ ), and red zinc oxide (zincite,  $ZnO$ ). Franklinite and willemite are ores of zinc containing manganese and iron. Gahnite has the composition  $ZnAl_2O_4$ .

Zinc ores are found in Germany, Italy, France, Greece, Spain, Austria-Hungary, Belgium, England, and the United States. Missouri and Kansas contain large deposits of the sulphide, while the other ores occur chiefly in New Jersey. About 200,000 tons of zinc are produced in the United States annually, and over 60 per cent comes from Missouri-Kansas. This amount is about one-third of the world's production.

**Metallurgy of Zinc.** — Zinc is easily smelted. The ores are first roasted to change them into the oxide, thus —

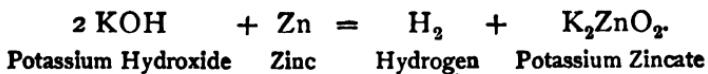


## Magnesium, Zinc, Cadmium, and Mercury. 335



The oxide is then reduced by heating it with charcoal. This operation is conducted in earthenware tubes or fire-clay crucibles connected with iron receivers into which the zinc vapor passes; at first it condenses as a powder known as **zinc dust**, somewhat as sulphur forms flowers of sulphur; but it finally condenses as a liquid, which is drawn off at intervals and cast into bars or plates. The impure zinc thus obtained is called **spelter**; it is freed from carbon, lead, iron, cadmium, and arsenic by repeated distillation, often under reduced pressure.

**Properties of Zinc.** — Zinc is a bluish white, lustrous metal. Its physical properties vary with the temperature. At ordinary temperatures it is brittle, but at  $100^\circ - 150^\circ\text{ C}$ . it is soft and may be rolled into sheets and drawn into wire, while its specific gravity rises from 6.9 to 7.2. Zinc which has been rolled or drawn does not become brittle upon cooling. At  $200^\circ\text{ C}$ . it again becomes brittle and can be easily pulverized. It melts at about  $420^\circ\text{ C}$ . and boils at about  $920^\circ\text{ C}$ . Heated in the air above its melting point, zinc burns with a bluish green flame, forming white zinc oxide ( $\text{ZnO}$ ). Zinc does not tarnish in dry air, but ordinarily it becomes coated with a dark film. Commercial zinc interacts with acids and usually liberates hydrogen. With hot solutions of sodium and potassium hydroxides, it forms **zincates** and liberates hydrogen, thus —



Pure zinc interacts with acids if in contact with a platinum wire, or if copper sulphate solution is added. Like copper,

zinc withdraws other metals (*e.g.* lead and mercury) from their solutions.

The vapor density of zinc requires the molecular weight 67.6. Since the atomic weight is 65.37, a molecule of the vapor contains only one atom.

**Uses of Zinc.**—Zinc in stick or plates is extensively used as the positive plate in electric batteries. Sheet zinc is used as a lining for tanks, and as the protective covering which is placed behind and beneath stoves. Iron dipped into melted zinc becomes coated with zinc and is called **galvanized iron**; it does not rust easily and is widely used for roofs, pipes, cornices, and water tanks. Telegraph wire is also galvanized. Zinc dust is used in the cyanide process of extracting gold and in many chemical experiments in the laboratory. Brass, German silver, and other **alloys contain zinc** (see Alloys of Copper). Antifriction metals, which are used for bearings, are alloys of zinc. Babbitt's metal, for example, contains 69 per cent of zinc, 19 of tin, 4 of copper, 3 of antimony, and 5 of lead.

**Compounds of Zinc.**—Native **zinc oxide** is red, owing to the presence of manganese, but the pure oxide is white when cold and yellow when hot. It is formed when zinc burns, and is manufactured in this way or by heating zinc carbonate. It is often called "zinc white" or "Chinese white," and is used to make a white paint which is not discolored by the atmosphere. Native **zinc sulphide** is yellow, brown, or black on account of impurities, but the pure sulphide is white. The latter is formed as a jellylike precipitate when hydrogen sulphide is passed into an alkaline solution of a zinc salt; it is decomposed by a mineral acid. Zinc sulphide is also used as a white pigment. **Zinc sulphate** is formed by the interaction of zinc and dilute sulphuric acid. Large quantities are made by roasting

the sulphide in a limited supply of oxygen and extracting the sulphate with water. It is a white, crystallized solid ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), which effloresces in the air, and when heated to  $100^\circ\text{ C}$ . loses most of its water of crystallization. The crystallized salt is called **white vitriol**. It is used in dyeing and calico printing, as a disinfectant, and as a medicine. It is poisonous, but can be safely used externally to relieve inflammation. **Zinc chloride** ( $\text{ZnCl}_2$ ) is a white, deliquescent solid, prepared by dissolving zinc in hydrochloric acid and evaporating the solution until a sample solidifies on cooling. It is used in surgery, and also as a constituent of a mixture for filling teeth; large quantities are used to preserve wood, especially railroad ties, from decay, nearly 1500 tons being annually consumed for this purpose. **Zinc hydroxide** ( $\text{Zn}(\text{OH})_2$ ) is formed by the interaction of sodium or potassium hydroxide and the solution of a zinc salt. An excess of the alkaline hydroxide changes the zinc hydroxide into a **zincate**.

**Tests for Zinc.**—The formation of the sulphide or hydroxide, as above described, serves as the **test for zinc**. A green incrustation is produced when zinc compounds are heated on charcoal and then moistened with a cobaltous nitrate solution.

**Cadmium**, Cd, is an uncommon metal, frequently found in zinc ores. It occurs native as a sulphide (greenockite,  $\text{CdS}$ ). It is white, lustrous, and rather soft. Its specific gravity is 8.6, and its melting point is about  $320^\circ\text{ C}$ . Cadmium is a constituent of certain fusible alloys (see Bismuth). Wood's metal contains 12 per cent of cadmium. The most important compound is cadmium sulphide ( $\text{CdS}$ ). This is a bright yellow solid, formed by adding hydrogen sulphide to the solution of a cadmium compound. It is used as an artist's color. Its formation also serves as the **test for cadmium**.

#### MERCURY.

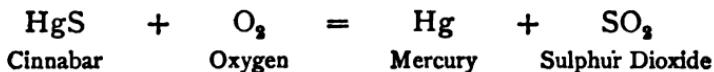
**Occurrence of Mercury.**—Native mercury is occasionally found in minute globules, but the most abundant ore

is mercuric sulphide (cinnabar, HgS). The ore is mined in Spain, Austria, Russia, Italy, and Mexico; in the United States large quantities are obtained in California, and deposits were recently opened in Texas.

The annual production of the United States for several years has been about 1500 tons.

Mercury has been known for ages as *quicksilver*. The Latin name, *hydrargyrum*, which gives us the symbol Hg, means literally "water silver," emphasizing the fact, so well known, that mercury looks like silver and flows like water.

**Preparation of Mercury.**—Mercury is readily prepared by roasting cinnabar in a current of air. Sulphur dioxide and mercury are formed, thus—



The sulphur dioxide is usually allowed to escape, but the mercury vapor is condensed by passing it into large chambers, or through pear-shaped retorts or pipes, called aludels (see Iodine). Crude mercury is freed from dirt and mechanical impurities by pressing it through linen or chamois leather, but it must be distilled to separate it from dissolved metals, such as lead or zinc. It can also be purified by treatment with dilute nitric acid. Mercury is sent into commerce in strong iron flasks, holding about 75 pounds.

**Properties of Mercury.**—Mercury is a bright, silvery metal, and is the only one which is liquid at ordinary temperatures. It solidifies at about  $-39.5^{\circ}\text{ C}$ . It is a heavy metal, the specific gravity being 13.59. It is slightly volatile even at ordinary temperatures, and the vapor is poisonous. Mercury does not tarnish in the air, unless sulphur compounds are present. At a high temperature, it combines slowly with oxygen to form the red oxide (HgO).

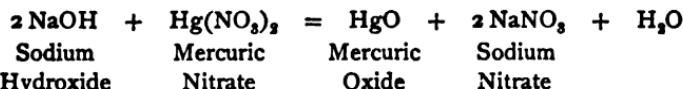
Hydrochloric acid and cold sulphuric acid do not affect it; hot concentrated sulphuric acid oxidizes it, and nitric acid changes it into nitrates.

The vapor density of mercury requires the molecular weight 198.72. Since the atomic weight is 200, a molecule of the vapor contains only one atom.

**Amalgams** are alloys of mercury with other metals. They are easily prepared by mixing the constituents. Sometimes the union is violent as in the preparation of **sodium amalgam**. **Amalgamated zinc** is usually used in electric batteries to prevent unnecessary loss of the zinc. **Tin amalgam** is sometimes used to coat mirrors. Amalgams of certain metals are used as a filling for teeth. Care should be taken, while handling mercury, not to let it come in contact with rings or jewelry, since **gold amalgam** is readily formed.

**Uses of Mercury.**—Mercury is used in making thermometers, barometers, and some kinds of air pumps. Its extensive use in extracting gold and silver has been mentioned (see *Amalgamation*). Large quantities are used in preparing certain medicines and explosives (*e.g.* fulminating mercury, which is used in cartridges).

**Compounds of Mercury.**—Mercury, like copper, forms two classes of compounds—the mercurous and the mercuric. **Mercuric oxide** ( $HgO$ ) is a red powder, produced by heating mercury in air or by heating a mixture of mercury and mercuric nitrate. As we have already seen, mercuric oxide is decomposed by heat into mercury and oxygen. A yellow variety is produced by the interaction of sodium hydroxide and a mercuric salt, thus—



**Mercurous chloride** ( $Hg_2Cl_2$  or  $HgCl$ ) is a white, tasteless powder, insoluble in water. It is formed when a chloride and mercurous nitrate

interact, but it is manufactured by heating a mixture of mercuric chloride and mercury. Under the name of calomel it is extensively used as a medicine. **Mercuric chloride** ( $HgCl_2$ ) is a white, crystalline solid, soluble in water and in alcohol. It is prepared by heating a mixture of mercuric sulphate and common salt. *It is a violent poison.* The best antidote is the white of a raw egg. The albumen forms an insoluble mass with the poison, which may then be removed mechanically from the stomach. The common name of mercuric chloride is **corrosive sublimate**. It has strong antiseptic properties, and is extensively used in surgery to protect wounds from the harmful action of germs; taxidermists sometimes use it to preserve skins, and it has many serviceable applications as a medicine and disinfectant. It is usually used as a dilute solution (1 part to 1000 parts of water). Native **mercuric sulphide** or cinnabar ( $HgS$ ) is a red, crystalline solid. When hydrogen sulphide is passed into a solution of a mercuric salt, mercuric sulphide is formed as a black powder; this variety, when heated, changes into red crystals.

**Vermilion** is artificial mercuric sulphide. It is manufactured either (1) by grinding together mercury and sulphur, and treating this mass with caustic potash solution, or (2) by heating mercury and sulphur in iron pans and subliming the black mass. In both processes the product must be carefully ground, washed, and dried. Chinese vermillion is the best quality. Vermilion has a brilliant red color, and, although expensive, is widely used to make red paint.

**Mercurous Nitrate** ( $HgNO_3$  or  $Hg_2(NO_3)_2$ ) and mercuric nitrate ( $Hg(NO_3)_2$ ) are prepared by treating mercury respectively with cold dilute nitric acid, and with hot concentrated nitric acid. They are white, crystalline solids.

#### EXERCISES.

1. Name the chief native compounds of magnesium. What proportion of the earth's crust is magnesium?
2. Describe the manufacture of magnesium by the electrolysis of carnallite.
3. Summarize the properties of magnesium. State its uses.
4. What is the formula and chemical name of magnesium? How is magnesia formed? State its properties and uses.
5. Describe the different varieties of magnesium sulphate. State the uses of Epsom salts.

## Magnesium, Zinc, Cadmium, and Mercury. 341

6. What is the formula of magnesium carbonate? What is (*a*) magnesite, (*b*) dolomite, (*c*) magnesia alba? For what is the last substance used?
7. Name the chief ores of zinc. Discuss their occurrence.
8. Describe the metallurgy of zinc. What is (*a*) zinc dust, and (*b*) spelter? How is zinc purified?
9. Summarize (*a*) the physical properties of zinc, and (*b*) the chemical properties.
10. State the uses of zinc.
11. Review the alloys of copper which also contain zinc. What alloys are largely zinc?
12. Describe native and pure zinc oxide. For what is the latter used?
13. Describe zinc sulphate. How is it formed and for what is it used?
14. Describe zinc chloride. For what is it used?
15. What are the tests for zinc?
16. State the properties and uses of (*a*) cadmium, and (*b*) cadmium sulphide.
17. What is the chief ore of mercury? Where is it found?
18. What is the symbol of mercury? What is the literal meaning of the word from which it is formed?
19. Describe the preparation and purification of mercury. How is it transported?
20. Summarize the properties of mercury.
21. What are amalgams? Name three, and state the use of each.
22. For what is mercury used?
23. Describe mercuric oxide. What historical interest has it?
24. Describe mercurous chloride. What is its commercial name? State its use.
25. Describe mercuric chloride. What is its commercial name? How does it differ from mercurous chloride? State its use.
26. What is the formula and chemical name of cinnabar? Describe cinnabar. What is vermillion? How is it manufactured? State its use.
27. What is (*a*) magnesia, (*b*) Epsom salts, (*c*) galvanized iron, (*d*) Chinese white, (*e*) white vitriol, (*f*) calomel, (*g*) corrosive sublimate?

**PROBLEMS.**

1. How much magnesium will be formed by heating 100 gm. of potassium with magnesium chloride? (Assume  $K_2 + MgCl_2 = Mg + 2 KCl$ .)
2. What is the per cent of magnesium in (a) magnesite ( $MgCO_3$ ), (b) dolomite ( $MgCa(CO_3)_2$ ), (c) Epsom salts ( $MgSO_4 \cdot 7 H_2O$ )?
3. What is the per cent of zinc in (a) zinc sulphate ( $ZnSO_4$ ), (b) zinc sulphide ( $ZnS$ ), (c) zinc chloride ( $ZnCl_2$ ), (d) zinc oxide ( $ZnO$ )?
4. How much zinc sulphate can be prepared from 65 gm. of zinc? From 130 gm.? From 720 gm.?
5. How much mercury is formed by decomposing 400 gm. of cinnabar? (Assume  $HgS + O_2 = Hg + SO_2$ )
6. What is the per cent of mercury in (a) mercuric oxide ( $HgO$ ), (b) calomel ( $Hg_2Cl_2$ ), (c) corrosive sublimate ( $HgCl_2$ )?

## CHAPTER XXV.

### ALUMINIUM.

**Occurrence.**—Aluminium does not occur free in nature, but its compounds are numerous, abundant, and widely distributed. About 8 per cent of the earth's crust is aluminium; it is, therefore, the most abundant metal. Many common rocks and minerals are silicates of aluminium and other metals, *e.g.* feldspar and mica, which make up a large part of granite and gneiss. Clay and slate are mainly silicate of aluminium, formed by the decomposition of complex aluminium minerals. Corundum and emery are aluminium oxide ( $\text{Al}_2\text{O}_3$ ) more or less impure. Bauxite is an hydroxide of aluminium ( $\text{H}_4\text{Al}_2\text{O}_5$ ). Cryolite is a fluoride of aluminium and sodium ( $\text{Na}_3\text{AlF}_6$ ).

Aluminium was first obtained as a fine powder by Wöhler in 1827. Deville, in 1854, prepared it in compact form and laid the foundation of the industry which is being developed by Hall.

Davy proposed the name *alumium*, i.e. *alum + ium*, to emphasize the relation of the metal to the well-known substance, alum. The word *alumium* was changed first to *aluminum* and then to *aluminium*. Some authorities derive the word *alumium* from the Latin word *alumen*, or from *alumina*, the common name of aluminium oxide.

**Metallurgy.**—Aluminium is obtained from its oxide ( $\text{Al}_2\text{O}_3$ ) by electrolysis. In the Hall process, which is typical, an open, iron box lined with carbon is made the cathode (Fig. 68). The anode consists of carbon bars hung from a copper rod, which can be lowered as the car-

bon is consumed. The process is essentially as follows: the bottom of the box is covered with cryolite, the anodes are lowered, and the box is then filled with cryolite. The current is turned on, and in its resisted passage through the cryolite enough heat is generated to melt the cryolite. Pure, dry aluminium oxide is now added. This is decom-

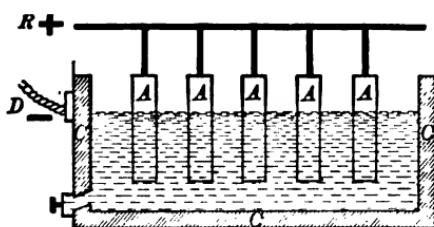


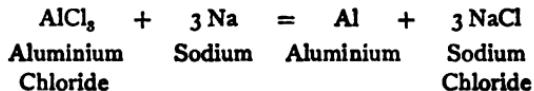
FIG. 68.—Apparatus for the manufacture of aluminium by the electrolysis of aluminium oxide. *CCC* is the iron box which serves as the cathode. *A*, *A*, etc. are carbon anodes attached to the copper rod, *R*.

posed into aluminium and oxygen. The oxygen unites with the carbon of the anodes, forming carbon monoxide, which burns or escapes. The molten aluminium falls to the bottom. The process is continuous, fresh aluminium oxide being

added and the molten aluminium being drawn off at intervals. The cryolite is unchanged, and merely acts as a solvent for the aluminium oxide.

The United States produces over 15,000,000 pounds of aluminium annually, and the output is steadily increasing. This was all produced at Niagara Falls. In the **Heroult process**, which is used in Europe and involves essentially the same principle as Hall's process, the aluminium is produced as an alloy (usually of copper).

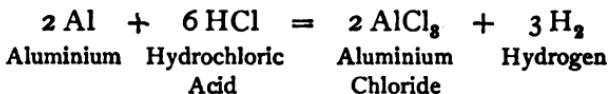
Aluminium was prepared until about 1885 by a complicated process. (1) Bauxite was changed into aluminium oxide free from iron by fusion with sodium carbonate and treatment with carbon dioxide. (2) The aluminium oxide was then changed into aluminium sodium chloride by fusion with sodium chloride and charcoal and subsequent treatment with chlorine. (3) This chloride was reduced by sodium, thus —



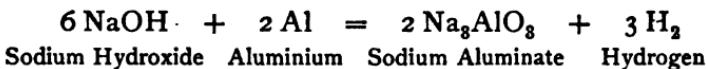
The sodium for this operation was prepared by the Castner process (see Sodium), and the two industries were developed simultaneously.

The extensive application of the electrolytic method has reduced the price of aluminium from about \$12 a pound during 1862-1887 to about 30 cents at the present time.

**Properties.**— Aluminium is a bluish white metal. It is very light compared with other common metals, since its specific gravity is only about 2.6; this value is one third that of iron. It is ductile and malleable, and is often sold in the form of wire and sheets; it must be annealed frequently during the hammering or drawing. It is a good conductor of heat and electricity. Its tensile strength is about as great as that of cast iron. It melts at about 660° C., and may be cast and welded, but not readily soldered so as to produce a permanent joint. The cap of the Washington Monument is a casting of aluminium which weighs about eight and a half pounds. Pure aluminium is only very slightly oxidized by air. Hydrochloric acid changes it into aluminium chloride, thus—



Under ordinary conditions nitric and sulphuric acids do not affect it. Sodium and potassium hydroxides change it into aluminates, thus—



The properties of aluminium are modified by the presence of impurities. The usual impurities are iron, other metals, and silicon. Some of these, especially the iron and silicon, come from the raw products used in its manufacture. They tend to make the metal harder and more active chemically, but less malleable, ductile, and tenacious. If it were not for the presence of these impurities in clay, this substance would be a cheap and inexhaustible source of aluminium.

**Uses.**—The varied properties of aluminium adapt it to numerous uses. It is made into the metallic parts of military outfits, caps for fruit jars, surgical instruments, cooking utensils, tubes, the framework and fittings of boats and air ships, telephone receivers, scientific apparatus, parts of opera glasses and telescopes, the framework of cameras, stock patterns for foundry work, and hardware samples. Its attractive appearance has led to its extensive use as an ornamental metal, both in interior decorative work and in numerous small objects, such as trays, picture frames, hairpins, and combs. Aluminium leaf is used for decorating book covers and signs; the powder is likewise used as a protective and attractive coating for letter boxes, steam pipes, lamp-posts, radiators, smokestacks, and other metal objects exposed to heat or the weather. During the last few years aluminium wire has come into use as a conductor of electricity. Considerable aluminium powder is used to reduce oxides, to make iron and steel more fluid, and to weld and repair iron pipes, rails, and rods. These mixtures of aluminium and oxides are called thermit.

**Alloys.**—The alloy of aluminium and copper—aluminium bronze—has been described (see Alloys of Copper). **Magnalium** is a recent alloy containing from 75 to 90 per cent of aluminium, the rest being magnesium.

**Aluminium Oxide**,  $\text{Al}_2\text{O}_3$ , is the only oxide of aluminium. It is often called **alumina**, as silicon dioxide is called silica. Its native forms, **corundum** and **emery**, are found in Massachusetts, New Jersey, Georgia, Pennsylvania, North Carolina, and Canada; large quantities come from Asia Minor and the islands near Greece. Emery is extremely hard, and is used in various forms—powder, cloth, paper, and wheels—to grind and polish hard metals, plate

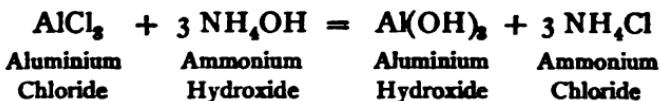
glass, etc. The crystallized varieties of aluminium oxide are usually known as corundum, and the transparent, colored kinds have long been prized as gems (see below).

Alumina may be prepared by burning the metal or by heating its hydroxide. Thus prepared, it is a white powder, insoluble in water, but soluble in acids and in the caustic alkalies. It melts in the oxyhydrogen flame, and in the electric furnace. Heating lessens its chemical activity. When alumina or any other compound of aluminium is heated, then cooled and moistened with cobaltous nitrate solution and heated again, the mass turns a beautiful blue color. This is a test for aluminium.

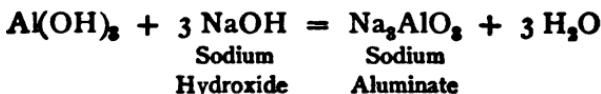
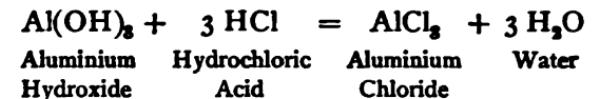
Artificial alumina is manufactured in the electric furnace. It is used as an abrasive and is called alundum.

**Gems containing Aluminium.**—Corundum ( $\text{Al}_2\text{O}_3$ ) has long been found as crystals in Ceylon, Siam, Burma, and other places in the Orient. The color is due to traces of impurities, usually oxides of metals. The sapphire is blue, and the ruby is red. The Oriental topaz is yellow, the Oriental amethyst is purple, and the Oriental emerald is green. Montana furnishes many sapphires, the annual output being valued at \$90,000. These gems may be artificially produced by dissolving alumina in a fused substance, adding an oxide to secure the desired color, and then allowing the alumina to crystallize. Spinels are complex compounds of aluminium. The typical or ruby spinel is magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ ). It resembles the true ruby. Other spinels differ from the ruby spinel both in color and in composition. Turquoise is a complex aluminium phosphate containing traces of copper. It has a beautiful robin's-egg-blue color, is compact, and may be worked into various shapes. Formerly turquoise came almost exclusively from Persia, but now New Mexico meets all demands. Nearly \$120,000 worth of turquoise are mined annually in that state. Topaz is a complex aluminium silicate containing fluorine. It is usually pale yellow, and is found in many localities. Emerald is, next to diamond and ruby, the most precious gem. It is an aluminium silicate containing the rare element beryllium. The finest specimens have a deep emerald-green color and come from Colombia, South America. Garnet is a complex silicate of aluminium and another metal, especially calcium, magnesium, iron, or manganese. The kind used as a gem has a deep red color and is rather abundant.

**Aluminium Hydroxide**,  $\text{Al}(\text{OH})_3$ , is a white, jellylike solid formed by adding an hydroxide to the solution of an aluminium salt, thus —



It is insoluble in water. It interacts with strong acids and with alkalies (except ammonium hydroxide), forming respectively aluminium salts and aluminates. Thus —



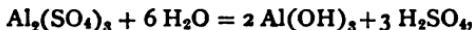
Aluminium hydroxide is also formed by the interaction of sodium carbonate or ammonium sulphide and an aluminium salt solution, because aluminium hydroxide is such a feeble base that it cannot form salts with weak acids like carbonic and hydrosulphuric ( $\text{H}_2\text{S}$ ). **Bauxite** is native aluminium hydroxide which contains ferric oxide and silica as impurities.

**Aluminium Sulphate**,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ , is a white, crystalline solid. The commercial salt has a variable composition; and, if pure, it dissolves readily and completely in water. It is extensively used in dyeing and paper making, and in preparing other aluminium compounds.

Aluminium sulphate is prepared from pure clay, bauxite, or cryolite. If clay or bauxite is heated with sulphuric acid and then allowed to cool, the product is impure aluminium sulphate, known as "alum cake," or, if much iron is present, as "alumino ferric cake." It is used to purify sewage and for other purposes where iron and the other impurities do no harm. Purer aluminium sulphate is prepared by heating

bauxite with soda ash, extracting the sodium aluminate formed with water, and precipitating the aluminium as the hydroxide with carbon dioxide gas. The relatively pure hydroxide is then changed into sulphate by treatment with sulphuric acid.

A solution of aluminium sulphate has an acid reaction on account of hydrolysis; the equation for the hydrolysis is —



the acid reaction being due to the hydrogen ions liberated by the ionization of the sulphuric acid.

**Alum.**—When solutions of aluminium sulphate and potassium sulphate are mixed and concentrated by evaporation, transparent, colorless, glassy crystals are deposited. This solid is **potassium alum**, or simply **alum**. It has the composition represented by the formula,  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$ , or  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ , and is sometimes called a double salt. It is the type of a class of similar salts called **alums**, which can be formed by crystallization from a mixture of aluminium sulphate and an alkaline sulphate. Alums are very soluble in water, and their solutions have an acid reaction and a sweetish, puckery taste. They crystallize alike, and contain twenty-four molecules of water of crystallization. When heated, alums lose their water of crystallization and some sulphuric acid, and fall to a white powder or porous mass known as **burnt alum**. Potassium alum is the most common, but ammonium and sodium alums are manufactured and used. Sodium alum is an ingredient of some baking powders. Burnt alum finds application as a medicine. Alum has been largely displaced by "concentrated alum," but the real alum is still used in dyeing and printing cloth, in tanning and paper making, in purifying water and sewage, as a medicine, for hardening plaster, in making wood and cloth fire-proof, and in preparing other aluminium compounds.

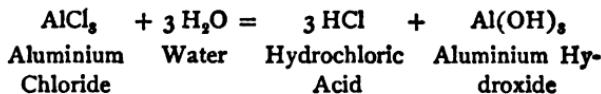
Alum was known to the ancients, who used it in dyeing and tanning, and as a medicine. It was first manufactured in Europe, about the thirteenth century, from native alunite, which is an impure sulphate of aluminium, potassium, and iron. Alunite and alum slates or shales are now used to some extent, but most of the alum is made from bauxite. Not all alums contain aluminium. This metal may be replaced by iron, chromium, manganese, or similar metals, producing salts which have the same general properties as ordinary alum. Hence the general formula of alums is  $M_2(SO_4)_3 \cdot X_2SO_4 \cdot 24 H_2O$ , in which M may be aluminium, iron, chromium, etc., and X a metal (or group) like potassium, sodium, ammonium. Chrome alum ( $K_2Cr_2(SO_4)_4 \cdot 24 H_2O$ ) belongs to this class. It is a purple, crystallized solid. The other alums have a limited, industrial application.

Alums and other aluminium salts are used as **mordants** in dyeing and calico printing. Some dyes must be fixed in the fabric by a metallic substance, otherwise the color would be easily removed. The cloth to be dyed or printed is impregnated or printed with the mordant, and then heated or treated with some substance to change the mordant into an insoluble compound. The mordanted cloth is next passed through a vat containing the solution of the dye, which unites chemically or mechanically (perhaps both) with the metallic compound, forming a *colored* compound. The latter is called a "lake"; it is relatively insoluble, and cannot be easily washed from the cloth, *i.e.* it is a fast color. Aluminium acetate or "red liquor" and aluminium sulphate, besides alum, are used as mordants for cotton, linen, and wool.

**Cryolite** is a white, glassy, crystallized solid. It often resembles clouded ice, and its name means "ice stone." Its composition corresponds to the formula  $Na_3AlF_6$  (or  $AlF_3 \cdot 3 NaF$ ). Small fragments melt easily, even in a candle flame, and color the Bunsen flame yellow. The only locality where it is found in commercial quantities is

southern Greenland, which yields annually about 10,000 tons. It is used not only in manufacturing aluminium, but as a source of alum and aluminium hydroxide, pure sodium carbonate and hydroxide, hydrofluoric acid, fluorides, and one kind of glass.

**Aluminium Chloride** when pure is a white powder, but it is often a yellowish, crystalline mass ( $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ ). It is prepared by heating powdered aluminium in chlorine, or by passing chlorine over a heated mixture of aluminium oxide and carbon. Exposed to the air, it absorbs moisture and gives off fumes of hydrochloric acid. It dissolves in water with evolution of heat, and if the solution is heated, hydrochloric acid is expelled, owing to the transformation of the chloride into the hydroxide, thus —



This salt is used in organic chemistry.

**Clay** is a more or less impure aluminium silicate, formed by the slow decomposition of rocks containing aluminium, especially feldspar. Pure feldspar is a silicate of aluminium and sodium or potassium. The products of its decomposition are chiefly an insoluble aluminium silicate and a soluble alkaline silicate. The latter is washed away. The aluminium silicate which remains is pure clay or **kaolin**. The latter is really a hydrous silicate, having the composition corresponding to the formula  $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$ . The composition of clay varies, because it is seldom formed from pure feldspar. Most kaolin contains particles of mica and quartz. Ordinary clay contains many impurities, *e.g.* carbonates of calcium and magnesium, quartz, and iron compounds. Kaolin is a white, powdery mass. It becomes slightly plastic when wet, and can therefore be molded into various shapes. Ordinary clay is very plastic when

wet, more easily fused than kaolin, but shrinks considerably when dried and burned; it also contains iron compounds, which color it gray, blue, yellow, brown, and red. All clays have a peculiar clayey odor when moist.

Clay is the basis of pottery, of which there are three general kinds: porcelain or china, stoneware, and earthenware.

**Porcelain** is the finest kind. It is made by heating to a high temperature a mixture of kaolin, fine sand, and some fusible substance, such as feldspar, chalk, or gypsum. The mass when cool is hard, dense, white, and translucent (if thin); it is not easily corroded by chemicals (except fused alkalies). Although it is not very porous, its surface is glazed, partly for protection, partly for ornament. This is done by coating it with a mixture similar to that used for making the porcelain but more easily fused, and then heating again so that the glaze will penetrate the surface. **Stoneware** is similar to porcelain, but coarser, because the materials are less carefully selected and prepared, and are not heated to such a high temperature. The best grades can hardly be distinguished from porcelain, but usually stoneware is much heavier and thicker. The cheaper kinds are made into jars, jugs, and bottles, especially large ones used in acid manufactories. Crockery is a fine grade of stoneware, though the best crockery is much like porcelain. If less pure, plastic clay is used and heated to a moderate temperature, the product is known as **earthenware**. This is a large class and includes majolica, tiles, terra cotta, jugs, flowerpots, clay tobacco pipes, drain pipe, and bricks. This ware is porous and is usually glazed by throwing salt into the baking oven just before the operation is over. The salt volatilizes and forms a fusible sodium aluminium silicate upon the surface. Cheap bricks are made from very impure clay, and their red color is due to iron oxides formed from the iron compounds in the unburned clay. Buff bricks are made from clay containing little or no iron, and clay containing silica yields fire-clay bricks, stove linings, retorts, and crucibles.

#### **EXERCISES.**

1. What is the symbol and atomic weight of aluminium?
2. Name several compounds of aluminium and discuss their occurrence. What proportion of the earth's crust is aluminium?

3. State briefly the history of aluminium.
4. Describe the metallurgy of aluminium by (a) the Hall process, (b) the Heroult process, (c) the older chemical method.
5. Discuss the production and cost of aluminium.
6. (a) Summarize the properties of aluminium. (b) State its uses.
- (c) Describe its alloys.
7. What is the formula and chemical name of alumina? Describe its preparation. State its properties and uses.
8. State the properties and uses of corundum and emery. Review carborundum (see Chapter X).
9. Name seven gems containing aluminium. Describe them.
10. Describe aluminium hydroxide. How does it interact with acids and with alkalies?
11. What is bauxite? For what is it used?
12. Describe aluminium sulphate. State its properties and uses. How is it prepared? What is "alum cake"? "Alumino ferric cake"? State their uses.
13. What is ordinary alum? How is it manufactured? State the general properties and uses of alums. What is (a) "concentrated alum," and (b) burnt alum?
14. Define a mordant. Describe its use. Name several mordants. What is (a) a "lake," (b) red liquor?
15. What is the general formula of an alum? What is chrome alum?
16. Where is cryolite found? State its properties and uses. What is its formula?
17. Describe the preparation and state the properties of aluminium chloride.
18. What is clay? How is it formed? What is kaolin? Describe (a) ordinary clay, and (b) kaolin.
19. Describe the manufacture of (a) porcelain, (b) stoneware, and (c) earthenware. Give an example of each. What is meant by glazing?

#### PROBLEMS.

What is the per cent of aluminium in (a) cryolite ( $\text{AlNa}_3\text{F}_6$ ), (b) turquoise ( $\text{Al}_2\text{P}_2\text{O}_8 \cdot \text{H}_2\text{Al}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ), (c) corundum ( $\text{Al}_2\text{O}_3$ ), (d) aluminium hydroxide ( $\text{Al}(\text{OH})_3$ )?

## CHAPTER XXVI.

### TIN AND LEAD.

TIN and lead are familiar metals. They have similar and useful properties, which give these metals and their compounds numerous applications.

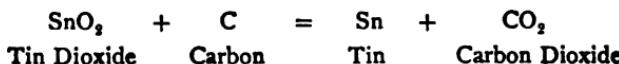
#### TIN.

**Occurrence of Tin.**—Metallic tin is rarely if ever found. Tin dioxide (cassiterite, tin stone,  $\text{SnO}_2$ ) is the only available ore. It is not widely distributed, but large deposits are found in England (at Cornwall), Germany (in Bohemia and Saxony), Australia, Tasmania, and the East Indian Islands, especially Banca and Billiton. A small quantity is found, but not mined, in the United States.

Tin is one of the oldest known metals. It is mentioned in the Pentateuch, and was obtained long before the Christian era by the Phoenicians from the British Isles, which were called Cassiterides (from the Greek word *kassiteros*, meaning tin). Many ancient bronzes contain tin. The alchemists called it Jupiter, and used the metal and its compounds.

The Latin word *stannum* gives us the symbol Sn and the terms *stannous* and *stannic*.

**Metallurgy of Tin.**—If the tin ore contains sulphur or arsenic, these impurities must be removed by roasting. The tin oxide is then reduced by heating it with coal in a reverberatory furnace; the simplest equation for this change is—



The molten tin which collects at the bottom of the furnace is drawn off and cast into bars or masses, which are often called **block tin**. Usually it is purified by melting it slowly on a hearth, inclined so that the more easily melted tin will flow down the hearth and leave the metallic impurities behind. This tin may be further purified by stirring the molten metal with a wooden pole, or by holding billets of wood beneath its surface. The impurities which are oxidized by the escaping gases collect as a scum on the surface and are removed.

**Properties of Tin.**—Tin is a white, lustrous metal, which does not tarnish easily in the air. It is soft and malleable, and can be readily cut and hammered. It is softer than zinc, but harder than lead. Its specific gravity is 7.3. Tin may be obtained in the crystalline form, and when a piece of such tin is bent it makes a crackling sound, which is caused by the friction of these crystals upon one another. It melts at about  $232^{\circ}$  C., and when heated to a higher temperature it burns, forming white tin oxide ( $\text{SnO}_2$ ). The physical properties of tin, like those of zinc, vary with the temperature. Concentrated hydrochloric acid changes it into stannous chloride ( $\text{SnCl}_2$ ); treated with hot concentrated sulphuric acid, it forms stannous sulphate ( $\text{SnSO}_4$ ) and sulphur dioxide; and commercial nitric acid oxidizes it, the white, solid product being known as **metastannic acid**. Zinc precipitates tin from its solutions as a grayish black, spongy mass, which is sometimes filled with bright scales.

**Uses of Tin.**—Tin is so permanent in air, weak acids (like vinegar and fruit acids), and alkalies that it is extensively used as a protective coating for metals. Ordinary **tinware** is sheet iron coated with tin. The tin plate (sheet tin, or simply "tin") is made by dipping very clean sheet iron into molten tin. Tacks, nails, and many small iron objects are similarly tinned. Copper coated with tin

is made into vessels for cooking, and brass coated with tin is made into pins. Large quantities of tin plate are used to cover roofs. Tinned iron does not rust until the tin is worn off and the iron exposed, and then the rusting proceeds rapidly. Tin is also hammered into thin sheets called **tin foil**, though much of the tin foil now used contains lead. Many useful alloys contain tin as an essential ingredient. During the last few years the annual consumption of tin has been about 100,000 tons.

**Alloys of tin** are described under **COPPER**. Those containing a minor percentage of tin are bronze, gun metal, bell metal, speculum metal, type metal, anti-friction metals, and fusible alloys. **Britannia metal** contains about 90 per cent tin, 8 per cent antimony, and the rest mainly copper. It is a white metal, and was formerly made into tableware. **White metal** contains less tin and more antimony than Britannia, though the composition varies. It resembles Britannia. The harder varieties of white metal are used as parts of machinery, and the softer kinds are made into ornaments and cheap jewelry. **Pewter** and **solder** contain varying proportions of tin and lead. Plumbers' solder, or soft solder, is about one third tin and two thirds lead. It is harder than either constituent, but it melts at a lower temperature. **Tin amalgam** is sometimes used to coat mirrors.

**Compounds of Tin.**—Tin forms two series of compounds, the stannous and the stannic. **Stannic oxide** ( $\text{SnO}_2$ ) has already been mentioned as the chief ore of tin, and as the product formed when tin is burned. The artificial oxide is faint yellow when hot and white when cold. The native oxide is a brown or black, lustrous, and often crystallized solid. Irregular pebbles called **stream tin** occur in some localities near rivers. **Stannous chloride** ( $\text{SnCl}_2$ ) is formed by the interaction of hydrochloric acid and tin. From the concentrated solution a greenish salt crystallizes ( $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ ), known as **tin crystals** or **salt of tin**.

Stannous chloride passes readily into stannic chloride ( $\text{SnCl}_4$ ) when added to mercuric chloride solution. The simplest equation for this change is—



By an extension of the simplest idea of oxidation and reduction, the stannous chloride in the change is said to be oxidized to stannic chloride, but it reduced the mercuric chloride to mercurous chloride. Stannous chloride is often used as a reducing agent and as a mordant in dyeing and calico printing. Crystallized stannic chloride ( $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ ), known commercially as **oxymuriate of tin**, is also used as a mordant. Tin mordants produce brilliant colors. Sodium stannate ( $\text{Na}_4\text{SnO}_3 \cdot 3 \text{H}_2\text{O}$ ) is extensively used to prepare cotton cloth for printing.

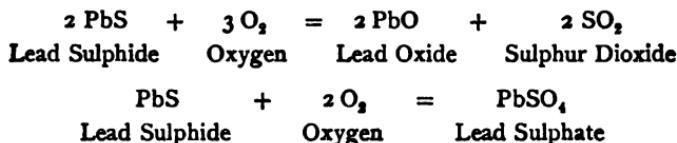
#### LEAD.

**Occurrence of Lead.** — Metallic lead is occasionally found in small quantities. The most abundant ore is lead sulphide (galena,  $\text{PbS}$ ). Other native compounds, formed by the alteration of galena, are the carbonate (cerussite,  $\text{PbCO}_3$ ), the sulphate (anglesite,  $\text{PbSO}_4$ ), and the phosphate (pyromorphite,  $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$ ). Lead compounds are widely distributed, but the source of commercial lead is the sulphide.

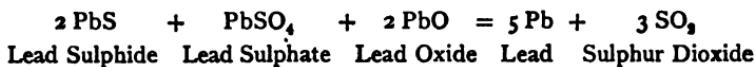
Lead has been used by civilized people since the dawn of history. The Chinese have used it for ages to line chests in which tea is stored and transported. The Romans, who obtained it from Spain, called it *plumbum nigrum*, *i.e.* black lead. The symbol Pb comes from *plumbum*. The ancients also used lead compounds (especially the carbonate and red oxide) as paints and cosmetics.

The annual production of lead has increased rapidly during the last few years, and it is now about 1,000,000 tons. This vast amount comes chiefly from the United States, Spain, Germany, Mexico, New South Wales, and England. The United States annually produces about 350,000 tons of lead from ores found mainly in the Middle West (Illinois, Iowa, Wisconsin, and Missouri), Colorado, Idaho, and Utah.

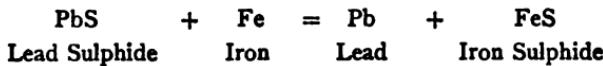
**Metallurgy of Lead.** — Lead is readily obtained from galena. (1) In the reduction process the ore is roasted in a reverberatory furnace until a part of the sulphide is changed into lead oxide and lead sulphate. The equations for these changes are —



The air is then shut off and the mixture of the three lead compounds is heated to a higher temperature. By this operation the lead sulphide interacts with the other lead compounds, forming lead and sulphur dioxide, thus —



(2) Ores poor in lead are sometimes reduced by roasting with iron, which combines with the sulphur, leaving the lead free, thus —



(3) In some refineries lead is obtained from galena by **electrolysis**. Crushed galena is made the cathode, dilute sulphuric acid is the electrolyte, and the bottom of the reduction pan is the anode. The sulphur is changed into hydrogen sulphide, which escapes into a combustion chamber where its sulphur is recovered or converted into sulphuric acid. The lead remains in the pan as a spongy mass. The silver, which remains in the lead obtained by reduction, is extracted by the Parkes process (see Silver).

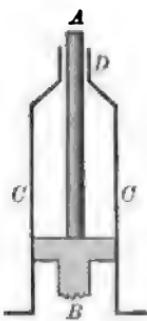
**Properties of Lead.** — Lead is a bluish metal. When scraped or cut, it has a brilliant luster, which soon disappears, owing to the formation of a film of oxide. This coating protects the lead from further change. It is a soft metal, and may be scratched with the finger nail. It discolors the hands, and when drawn across a rough surface it leaves a black mark. For this reason it is sometimes

called **black lead** (see Graphite). Lead is not tough enough to be readily hammered into foil or drawn into fine wire, but it can be rolled into sheets. It is a heavy metal, its specific gravity being 11.35; with the exception of mercury, it is the heaviest of the familiar metals. It melts at 326° C., or about 100° higher than tin and 100° lower than zinc. Lead, when heated strongly in air, changes into an oxide (mainly the monoxide, PbO). Hydrochloric and sulphuric acids have little effect upon compact lead. Nitric acid changes it into lead nitrate ( $Pb(NO_3)_2$ ). Acetic acid (or vinegar) and acids from fruits and vegetables change it into soluble, poisonous compounds; hence cheap tin-plated vessels, which sometimes contain lead, should never be used in cooking. Zinc and iron precipitate lead from its solutions as a grayish mass, which often has a beautiful treelike appearance.

**Lead in Drinking Water.**—Lead is slowly changed into soluble compounds by water containing carbon dioxide, ammonia, nitrates, or chlorides. But water containing sulphates or carbonates forms an insoluble coating on the lead, thus protecting it from further action. All lead salts are poisonous, and if taken into the system they will slowly accumulate and ultimately cause serious and dangerous illness. Water suspected of attacking lead should never be drunk after it has been standing very long in lead pipes, but should be allowed to flow until the pipe has been filled with fresh water. Sometimes the water cannot be drunk at all. The city of Lowell, Massachusetts, recently abandoned one source of its water supply because of the rapid solvent action of the water upon lead pipes.

**Uses of Lead.**—Lead is extensively used as pipe, because it can be made into indefinitely long pieces, which

can be easily bent, cut, and united (by solder). The pipe is made by forcing softened lead through a hole in a steel plate or by the apparatus shown in Figure 69. Lead pipe is not only used to convey water to and from parts of buildings,



in Figure 69. Lead pipe is not only used to convey water to and from parts of buildings, but as a sheath for copper wires, both overhead and underground. As sheet lead it is used to cover roofs and to line sinks, cisterns, and the cells employed in many electrolytic processes. The lead chambers and evaporating pans used in manufacturing sulphuric acid are made of sheet lead. Shot and bullets are lead (alloyed with a little arsenic). Spongy lead is used in preparing the plates of storage batteries.

**The Alloys of Lead** are important. **Type metal** contains 70 to 80 per cent lead; the other constituents are tin and antimony. The latter metal expands when it solidifies and makes the face of the type sharp and clear.

**Solder, pewter, and fusible alloys** contain lead as an essential constituent (see Alloys of Tin). Small quantities are found in brass and bronze.

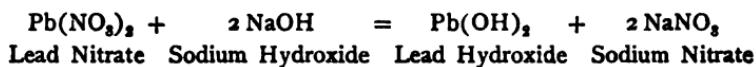
**Lead Oxides.** — There are three important oxides. **Lead monoxide** ( $PbO$ ) is a yellowish powder known as **massicot**, or a buff-colored crystalline mass called **litharge**. It is formed by heating lead above its melting point in a current of air. It is made this way, though considerable is obtained as a by-product in separating silver from lead (see Cupellation). Large quantities are used in preparing some oils and varnishes, flint glass, other lead compounds, and as a glaze. **Lead tetroxide** (**red lead**, **minium**,  $Pb_3O_4$ ) is a red powder, varying somewhat in color and

composition. It is prepared by heating lead (or lead monoxide) to about  $350^{\circ}\text{C}$ . It is used in making flint glass. Pure grades are made into artists' paint, but the cheap variety is used to paint structural iron work (bridges, gasometers, etc.), hulls of vessels, and agricultural implements. It is used in plumbing and gas fitting to make joints tight. **Orange mineral** has the same composition as red lead, and although its color is lighter, its uses are the same. **Lead dioxide** (lead peroxide,  $\text{PbO}_2$ ), is a brown powder formed by treating lead tetroxide with nitric acid. It is used in storage batteries.

**Lead Carbonate**,  $\text{PbCO}_3$ , is found native as the transparent, crystallized mineral **cerussite**. It is obtained as a white powder by adding ammonium carbonate solution to lead nitrate solution. Sodium and potassium carbonates, however, form basic lead carbonates, which have a composition depending upon the temperature. The most important of these basic carbonates has the composition corresponding to the formula  $2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , and is known as **white lead**. It is a heavy, white powder which mixes well with linseed oil, and is used extensively as a white paint and as the basis of many colored paints.

White lead is manufactured by several processes. The **Dutch process** is the oldest, having been used as early as 1622. It is essentially the same to-day, though many details have been improved. Perforated disks of lead are put in earthenware pots which have a separate compartment at the bottom, containing a weak solution of acetic acid (about as strong as vinegar). These pots are arranged in tiers in a large brick building, and spent tan bark is placed between each tier. The building is now closed except openings for the entrance and exit of air and steam. The heat volatilizes the acetic acid which changes the lead into a lead acetate. The tan bark ferments and liberates carbon dioxide, which changes the lead acetate into basic lead carbonate or white lead. The whole operation requires from sixty to one hundred days. The slowness is the chief objection to this process. In

the **German process** acetic acid vapor, steam, and carbon dioxide are forced into closed chambers in which sheets of lead are suspended. It requires about five weeks. In the **French process** basic lead carbonate is precipitated from a basic lead acetate by carbon dioxide. **Milner's process** is a modification of the French process. Both are quicker than the Dutch or German processes, but the product is not considered so good. An **electrolytic process** has recently been devised. The anode is lead, the cathode is copper, and the electrolyte is sodium nitrate solution. When the electric current is passed, (1) nitric acid is liberated at the anode, and changes the lead into lead nitrate, and (2) at the cathode sodium is formed, which decomposes the water, thereby forming sodium hydroxide. The lead nitrate and sodium hydroxide solutions interact, forming insoluble lead hydroxide and sodium nitrate, thus —



The sodium nitrate is left in the cell to be acted upon again, but the lead hydroxide is changed into lead carbonate by treatment with sodium bicarbonate. This process is rapid, and the product is claimed to be as good as white lead produced by other processes.

White paint turns dark, owing to the formation of lead sulphide, which is black. Its extensive use is largely due to its great covering power, *i.e.* a very thin layer produces a perfectly white surface, and therefore less paint is required for a given area. It is often adulterated with zinc oxide and barium sulphate; those are white solids, but they are cheaper and have less covering power.

**Lead Sulphide, PbS.** — Native lead sulphide is the mineral **galena**, the chief ore of lead. It resembles lead in

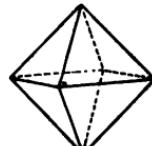
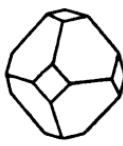
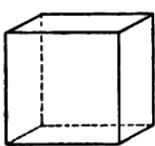


FIG. 70. — Galena crystals (cube, octahedron and cube, octahedron).

appearance, but is harder and is usually crystallized as cubes, octahedrons, or their combinations (Fig. 70). It

has perfect cubic cleavage, *i.e.* it breaks into cubes or fragments more or less rectangular. It is easily changed into lead by heating it alone or with sodium carbonate on charcoal. Lead sulphide, as prepared in the laboratory, is a black solid.

Black lead sulphide is readily precipitated from a lead salt solution by hydrogen sulphide. Its formation is the test for lead. It is changed into lead chloride by concentrated hydrochloric acid and into lead sulphate by concentrated nitric acid.

**Other Compounds of Lead**, which are important, are the chloride, sulphate, nitrate, chromate, and acetate. **Lead chloride** ( $PbCl_2$ ) is a white solid formed by adding hydrochloric acid or a soluble chloride to a cold solution of a lead salt. It dissolves in hot water. **Lead sulphate** ( $PbSO_4$ ) is a white solid, formed by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is very slightly soluble in water, but soluble in concentrated sulphuric acid, hence crude sulphuric acid often contains lead sulphate. **Lead nitrate** ( $Pb(NO_3)_2$ ) is a white crystallized solid formed by dissolving lead (or better, lead monoxide) in nitric acid. When heated, it decomposes into lead oxide ( $PbO$ ), nitrogen peroxide, and oxygen. **Lead acetate** ( $Pb(C_2H_4O_2)_2$ ) is a white, crystallized solid formed by the action of acetic acid upon lead or lead oxide ( $PbO$ ). It is very soluble in water and is often called "sugar of lead."

#### EXERCISES.

1. Name the chief ore of tin. Where is it found? What is "stream tin"?
2. Give briefly the history of tin. What is its symbol? Why?
3. Describe (*a*) the metallurgy of tin, and (*b*) its purification.
4. Summarize the properties of tin. State its uses.
5. What is "tin"? Block tin? Tin foil? Tinware? Sheet tin? Tin plate?
6. Describe three alloys which contain large proportions of tin. Name several alloys containing a minor proportion of tin.
7. Compare native and artificial tin oxide ( $SnO_2$ ).
8. What is the formula of (*a*) stannous chloride, and (*b*) stannic chloride? What is their chemical relation? State the use of each chloride. What other names has stannous chloride?

9. What is the most abundant ore of lead? Name other native compounds.
10. Give a brief history of lead. What is its symbol? Why?
11. Discuss the production of lead.
12. Describe the metallurgy of lead by (a) the reduction process, (b) roasting with iron, (c) electrolysis of galena.
13. Summarize the properties of lead.
14. State the uses of lead.
15. Discuss the relation of lead to water.
16. What is (a) type metal, (b) solder, (c) fusible alloy?
17. Give the name and formula of the oxides of lead.
18. Describe the preparation, and state the properties and uses of (a) litharge, (b) red lead, (c) lead peroxide.
19. What is white lead? Describe its preparation by (a) the Dutch method, and (b) electrolysis of sodium nitrate.
20. State the properties and uses of white lead.
21. What is the formula and chemical name of galena? Describe this mineral. Describe the corresponding artificial compound. What is the test for lead?
22. Describe the following salts of lead: (a) chloride, (b) sulphate, (c) nitrate, (d) acetate.

#### **PROBLEMS.**

1. What is the per cent of lead in (a) galena ( $PbS$ ), (b) cerussite ( $PbCO_3$ ), (c) anglesite ( $PbSO_4$ ), (d) lead acetate ( $Pb(C_2H_5O_2)_2 \cdot 3 H_2O$ )?
2. How much litharge may be made from 40.5 gm. of lead? (Assume  $Pb + O = PbO$ .)
3. What is the per cent of tin in (a) tinstone ( $SnO_2$ ), (b) stannous chloride ( $SnCl_2$ ), (c) stannic chloride ( $SnCl_4$ )?

## CHAPTER XXVII.

### CHROMIUM AND MANGANESE.

THESE elements do not belong to the same group, but they have several common properties and form analogous compounds.

#### CHROMIUM.

**Occurrence of Chromium.**—Metallic chromium is never found free. Its chief ore is an oxide (chromite, chrome iron ore,  $\text{FeCr}_2\text{O}_4$ ). Native lead chromate (crocoite or crocoisite,  $\text{PbCrO}_4$ ) is less common. Traces of chromium occur in many green minerals and rocks, e.g. emerald and serpentine, and verde antique marble.

Chromite is mined chiefly in Greece, New Caledonia, New South Wales, Turkey, and Canada. The total annual production is about 30,000 tons.

The word *chromium* comes from the Greek word *chroma*, meaning color, and emphasizes the fact that most chromium compounds have decided colors.

**Preparation, Properties, and Uses.**—Chromium was a rare metal until Moissan prepared it, in 1894, in the electric furnace. Now it is produced in quantities by heating a mixture of chromite and carbon in an electric furnace. The crude chromium is refined by fusing it with lime. Very pure chromium is also prepared by reducing chromic oxide with aluminium powder.

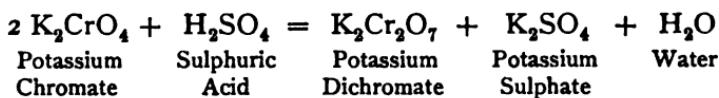
Chromium is a lustrous gray metal. It takes a good polish, which is not removed by exposure to air. It is hard, but it can be filed and polished without difficulty. Its specific gravity is about 6.9. It is not attracted by a magnet. It can be fused only in the electric furnace.

Chromium is used to harden the steel, which is to be made into armor, projectiles, safes, and vaults, and parts of machines used to

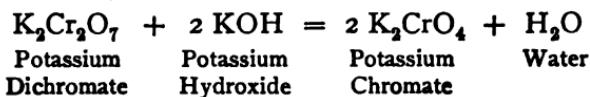
crush gold-bearing quartz. This hardened steel is called **chrome steel**. The commercial form of chromium is an alloy of 65 to 80 per cent chromium, a little carbon, and the rest iron; this alloy is called **ferro-chrome**.

**Compounds of Chromium** are numerous, some are complex, many pass readily into one another, and a few have industrial applications. The most important are potassium chromate, potassium dichromate, chrome alum, and lead chromate.

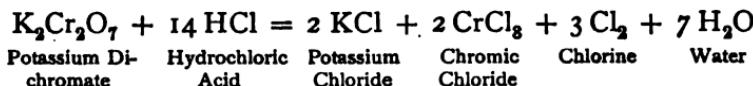
**Potassium Chromate** ( $K_2CrO_4$ ) and **Potassium Dichromate** (or **Bichromate**,  $K_2Cr_2O_7$ ). — These compounds are manufactured from chrome iron ore. The crushed ore is mixed with lime and potassium carbonate, and roasted in a reverberatory furnace; air is freely admitted and the mass is frequently raked. By this operation the ore is oxidized into a mixture of calcium and potassium chromates. The mass is cooled, pulverized, and treated with a hot solution of potassium sulphate, which changes the calcium chromate into potassium chromate. The clear, saturated solution of potassium chromate is changed by sulphuric acid into potassium dichromate; the latter is purified by recrystallization from water. **Potassium chromate** is a lemon-yellow, crystallized solid, very soluble in water. Acids change it into the dichromate, thus —



**Potassium Dichromate** is a red solid which forms large crystals. It is less soluble in water than potassium chromate. Alkalies change it into a chromate, thus —



Potassium dichromate is used in dyeing, calico printing, and tanning, in bleaching oils, and in manufacturing other chromium compounds and dyestuffs. Its uses depend mainly upon the fact that it is an oxidizing agent. When hydrochloric acid is added to potassium dichromate, oxygen from the dichromate withdraws hydrogen from the acid and liberates free chlorine, thus—



If an oxidizable substance is present, such as organic matter, alcohol, or a ferrous compound, it is quickly oxidized.

Potassium chromate is also formed as a yellow mass by fusing on porcelain or platinum a mixture of a chromium compound, potassium carbonate, and potassium nitrate. When the mass is boiled with acetic acid to decompose the carbonate and expel carbon dioxide, and then added to a lead salt solution, yellow lead chromate is formed. This experiment is often used as a test for chromium.

**Chrome Alum**,  $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$ , is a purple, crystallized solid. It is analogous in composition and similar in properties to ordinary alum, but it contains chromium instead of aluminium. It can be prepared by mixing potassium and chromium sulphates in the proper proportion, or by passing sulphur dioxide into a solution of potassium dichromate containing sulphuric acid. The commercial substance is a by-product obtained in the manufacture of alizarine, a dye which yields magnificent colors. Chrome alum is used as a mordant in dyeing and calico printing, and in tanning.

**Lead Chromate**,  $\text{PbCrO}_4$ , is a bright yellow solid, formed by adding potassium chromate or dichromate to a solution of a lead salt. It is known as **chrome yellow** and is used as the basis of yellow paint. When boiled with sodium

hydroxide (or any other alkali), lead chromate is changed into a complex chromate called **chrome red** or **chrome orange**, depending upon the color.

The precipitation of lead chromate by the interaction of a dissolved lead salt and a dissolved chromate (or dichromate) is a **test for chromium**.

**Chromium forms Three Series of Compounds**, — the chromous, the chromic, and the chromates. Chromous compounds may be regarded as derived from **chromous oxide** ( $\text{CrO}$ ). As a class they are so easily oxidized into chromic compounds that they are hard to prepare and keep. In chromic compounds, chromium acts as a metal. They may be regarded as derivatives of **chromic oxide** ( $\text{Cr}_2\text{O}_3$ ). This is a bright green powder prepared by heating chromic hydroxide ( $\text{Cr}(\text{OH})_3$ ), and is the basis of chrome green pigments used to color glass and porcelain. When chromium compounds are heated with borax they color the bead green, owing to the formation of this oxide. If potassium dichromate and boric acid are mixed and heated, and then treated with water, a hydrated chromic oxide is formed called **Guignet's green** ( $\text{Cr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ ) ; it gives a permanent color and is extensively used. There are several **chromic hydroxides**. The typical one has the composition represented by the formula  $\text{Cr}(\text{OH})_3$ . It is a bluish solid formed by the interaction of a chromic compound (*e.g.* chrome alum) and an alkaline hydroxide, carbonate, or sulphide. The chromic hydroxide, which is always precipitated, is soluble in an excess of sodium (or potassium) hydroxide. That is, it is changed into a soluble chromite, just as aluminium hydroxide forms soluble aluminates. Unlike aluminates, however, the chromites are changed back into chromic hydroxide by boiling. **Chromites** may be regarded as salts of an acid having the composition corresponding to  $\text{HCrO}_2$ ; native chromite ( $\text{FeCr}_2\text{O}_4$  or  $\text{Fe}(\text{CrO}_2)_3$ ) is an iron salt of this acid. Other chromic salts are **chromic chloride** ( $\text{CrCl}_3$ ), **chromic sulphate** ( $\text{Cr}_2(\text{SO}_4)_3$ ), and **potassium chromium sulphate or chrome alum** (see above). **Chromates and dichromates** start theoretically from chromium trioxide ( $\text{CrO}_3$ ). This is the anhydride of the hypothetical chromic acid ( $\text{H}_2\text{CrO}_4$ ). In this class of compounds chromium acts as a non-metal, just like sulphur in sulphuric acid. When concentrated sulphuric acid is added to a saturated solution of potassium dichromate (or chromate), chromium trioxide separates as long, bright red crystals. It is a vigorous oxidizing agent.

**Molybdenum (Mo), Tungsten (W), and Uranium (U)** are rare metallic elements related to chromium. Most of their compounds have only scientific interest, though some have analytical or industrial uses. Ammonium molybdate ( $(\text{NH}_4)_2\text{MoO}_4$ ) is used in the laboratory to determine the amount of phosphorus in fertilizers and iron. Tungsten is used to harden steel, and sodium tungstate for making cloth fireproof. Salts of uranium are used to color glass. Such glass is green by transmitted light, but yellow by reflected light.

#### MANGANESE.

**Occurrence of Manganese.** — This elementary metal is not found free in nature, but its oxides are widely distributed and rather abundant. The chief compound is manganese dioxide (pyrolusite,  $\text{MnO}_2$ ).

Other native compounds of manganese are braunite ( $\text{Mn}_2\text{O}_5$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), manganite ( $\text{MnO}(\text{OH})$  or  $\text{MnO}_2\text{H}$ ), and rhodocroisite ( $\text{MnCO}_3$ ).

Manganese ores are usually impure, and their value is estimated by determining the actual per cent of manganese dioxide they contain. The largest producers of manganese ore are Russia, the United States, Spain, India, and Brazil. The output in the United States comes chiefly from Georgia, Virginia, and Utah, though poor ores are mined in Colorado and the Lake Superior region. The United States produces only a small fraction of the amount annually consumed, and imports nearly 175,000 tons.

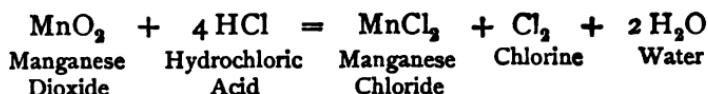
**Preparation, Properties, and Uses of Manganese.** — Manganese is prepared by heating manganese dioxide with charcoal in an electric furnace, or by reducing the oxide with aluminium powder.

The metal is grayish, hard, and brittle. Its brilliant luster soon disappears in moist air, and the powdered metal decomposes boiling water. It dissolves in dilute acids.

**Alloys of Manganese** and iron are extensively used in the manufacture of Bessemer steel (see Steel). Spiegel iron contains from 5 to 20 per cent of manganese, while ferromanganese contains 20 per cent or more.

**Manganese Dioxide,  $\text{MnO}_2$ ,** is the most abundant and important compound. It is a soft, black solid, and is often

called **black oxide of manganese**. When heated it yields oxygen; and when heated with hydrochloric acid the two compounds interact, forming manganous chloride, chlorine, and water, thus —



It colors glass and borax a beautiful amethyst, and is often added to common glass to neutralize the green color. Enormous quantities are used in the manufacture of oxygen, chlorine, glass, and manganese alloys and compounds.

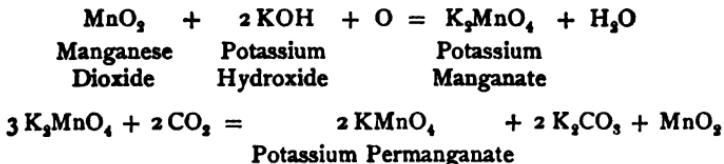
The manganese dioxide used in the manufacture of chlorine is recovered by the **Weldon process**. The impure manganous chloride solution from the chlorine still is treated with calcium carbonate to neutralize free acid and precipitate any iron present. Lime is added to the clear solution of manganous chloride, and air is blown into the mixture. The manganous chloride is changed into manganous hydroxide ( $\text{Mn}(\text{OH})_2$ ), which interacts with the oxygen (of the air) and lime, forming chiefly calcium manganite ( $\text{CaMnO}_3$ , or  $\text{CaO} \cdot \text{MnO}_2$ ). After this mixture has settled, the calcium chloride is drawn off, and the manganese compound, which is called "Weldon mud," is used to generate more chlorine.

Manganese dioxide was used by the ancients to decolorize glass, but its nature was misunderstood. They confused it with an iron oxide called **magnesia stone**, and the alchemists in the Middle Ages gave the name **magnesia** to this manganese dioxide. Later they called it **magnesia nigra**, or black magnesia, to distinguish it from **magnesia alba**, or white magnesia ( $\text{MgO}$ ), supposing that the two were related. Manganese was isolated in 1774, and later was given the specific name **manganesium**, which was soon shortened to **manganese**.

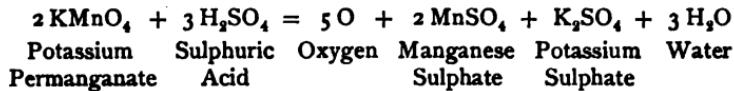
**Potassium Permanganate**,  $\text{KMnO}_4$ , is a dark purple, glistening, crystallized solid, though the crystals sometimes appear black, with a greenish luster. It is very soluble in water, and the solution is red, purple, or black, according to the concentration. Potassium permanganate gives up its oxygen readily and is used as an oxidizing agent in the

laboratory and on a large scale to purify stagnant water and sewage. It is such a powerful oxidizing agent that it cannot be filtered through paper, but only through asbestos or spun glass. It is also used as a disinfectant, as a medicine, in bleaching and dyeing, in coloring wood brown, and in purifying gases, such as hydrogen, ammonia, and carbon dioxide.

Potassium permanganate is manufactured by oxidizing a mixture of manganese dioxide and potassium hydroxide, and treating the resulting potassium manganate with sulphuric acid, carbon dioxide, or chlorine. The essential reactions are represented thus—



The uses of potassium permanganate depend mainly upon its oxidizing power. With sulphuric acid the action is represented thus—



The liberated oxygen attacks at once any organic matter present, and the solution becomes brown or colorless, owing to the decomposition of the potassium permanganate into colorless compounds.

**Compounds of Manganese**, like those of chromium, are numerous, often complex, and closely related. There are four **oxides** besides manganese dioxide. Three **manganous compounds** are important, the chloride ( $\text{MnCl}_2$ ), the sulphate ( $\text{MnSO}_4$ ), and the sulphide ( $\text{MnS}$ ). The chloride and sulphate are pink, crystallized salts, and the sulphide is a flesh-colored precipitate formed by adding ammonium sulphide to the solution of a manganous salt, thus distinguishing it from all other sulphides. **Manganates** are salts of the hypothetical manganic acid ( $\text{H}_2\text{MnO}_4$ ). They are analogous to chromates, and the manganese in them acts as a non-metal. **Potassium manganate** is obtained as a green mass by fusing a mixture of a manganese compound, potassium

hydroxide (or carbonate), and potassium nitrate. Its formation on a small scale constitutes the test for manganese. Sodium manganate ( $\text{Na}_2\text{MnO}_4$ ) is used in solution of a disinfectant.

**Radium and Radio-Activity.**—Radium, Ra, is an element whose compounds are obtained by a tedious process from pitchblende and other minerals containing uranium. Radium itself has not yet been isolated, but its chloride and bromide have been prepared and studied, especially by Mme. Curie. Radium compounds color the Bunsen flame red, are naturally phosphorescent, and produce phosphorescence in diamond and other substances. Certain properties are conspicuously different from those exhibited by most substances. Thus, radium compounds spontaneously evolve relatively large quantities of heat, affect a photographic plate, and discharge an electroscope. These properties are called radio-active properties. Uranium and thorium compounds behave similarly to radium compounds.

Radio-active phenomena are due to the spontaneous emission of two kinds of very small particles designated as  $\alpha$  and  $\beta$  and to disturbances in the ether similar to light—the so-called  $\gamma$ -radiation. Each kind of particle or radiation produces a relatively different effect. It has been found by experiment that radio-active substances undergo continuous changes, which give rise to new substances. One of these new substances is called radium emanation; its decomposition, or "decay," as it is called, yields helium as one product. Radio-activity is still under investigation and many results await interpretation. The following, however, seem to be well established: (1) uranium, thorium, radium, and possibly other elements are undergoing spontaneous decomposition; (2) helium is formed by the decomposition of elements having a higher atomic weight; (3) the atom as postulated by chemists is unstable and in some cases tends to assume a more stable form; (4) enormous quantities of energy are involved in radio-active transformations.

#### PROBLEMS.

1. What is the per cent of chromium in (a) lead chromate ( $\text{PbCrO}_4$ ), (b) chrome ironstone ( $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ ), (c) chromic oxide ( $\text{Cr}_2\text{O}_3$ )?
2. What is the per cent of manganese in (a) manganese dioxide ( $\text{MnO}_2$ ), (b) manganese sulphide ( $\text{MnS}$ ), (c) manganese alum ( $\text{K}_2\text{Mn}_2(\text{SO}_4)_4 \cdot 24 \text{H}_2\text{O}$ )?
3. How much manganese ore containing 85 per cent of manganese dioxide is needed to prepare 300 lb. of chlorine?

## CHAPTER XXVIII.

### IRON, NICKEL, AND COBALT.

**Introduction.** — These three elements form a natural group. Their properties are similar. Cobalt and nickel are very closely related and are seldom found alone. Iron resembles manganese and chromium.

#### IRON.

Iron is the most useful of all metals. It has been known for ages, and has been indispensable in the development of the human race.

The symbol of iron, Fe, is from the Latin word *ferrum*. From *ferrum* are derived the forms ferri- and ferro- (found in such words as ferricyanide, ferromanganese, ferrocyanide, etc.), and the terms *ferrous* and *ferric*.

**Occurrence of Iron.** — Uncombined iron is found only in meteorites, which fall upon the earth from remote regions in space, and in a very few rocks. Combined iron is abundant and widely distributed. It is found in most rocks and many minerals, in the soil, in springs and natural waters, in chlorophyll — the green coloring matter of plants, — and in haemoglobin — the red coloring matter of blood. The chief ores of iron are hematite ( $\text{Fe}_2\text{O}_3$ ), limonite ( $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and siderite ( $\text{FeCO}_3$ ).

Other abundant compounds of iron not used as a source of the metal are pyrites ( $\text{FeS}_2$ ), pyrrhotite (varying from  $\text{Fe}_6\text{S}_7$  to  $\text{Fe}_{11}\text{S}_{12}$ ), and the copper-iron sulphides (chalcopyrite,  $\text{CuFeS}_2$ , and bornite,  $\text{Cu}_5\text{FeS}_4$ ).

The United States leads the world in the production of iron ore, the annual output for the last few years being over 50,000,000 tons. This vast quantity comes from twenty-five different states, but the bulk is mined in Minnesota, Michigan, Alabama, Wisconsin, Tennessee, Virginia and West Virginia, and Colorado. The most abundant ore is the red hematite, which comes chiefly from the Lake Superior region (Fig. 71); large quantities are mined in Alabama and Tennessee. The latter states, together with Virginia and West Virginia, furnish most of the limonite or brown iron ore. Pennsylvania, New Jersey, and New York contribute most of the magnetite, though some is mined also in

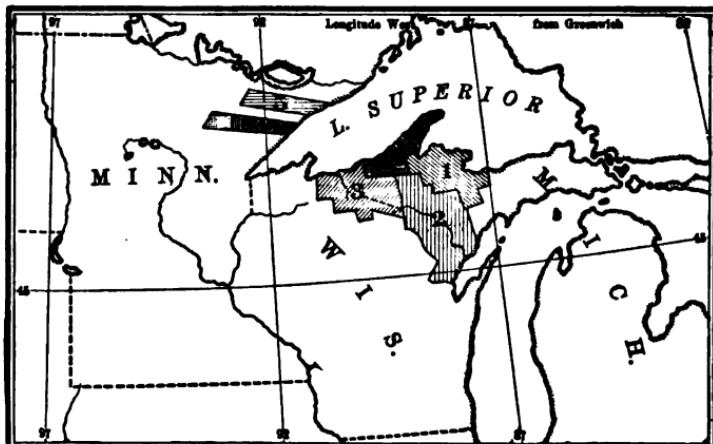


FIG. 71.—Deposits of iron and copper near Lake Superior. No. 4 is the copper region. The iron regions, known as ranges, are Marquette (1), Menominee (2), Gogebic (3), Vermilion (5), Mesabi (6).

Michigan. The carbonate ores, which constitute less than one per cent of the output, come mainly from Ohio, Maryland, and New York. Improvements in the machinery and methods used in mining and transporting iron ore have reduced its cost and facilitated its production. Thus, at an incredibly small expense, ore from the Lake Superior region is raised from open pits by steam shovels, dumped into large cars, carried to shipping ports on the lakes, dumped again into huge bunkers, dropped down chutes into big freight steamers (many of which hold 6000 tons), which carry it to South Chicago and Milwaukee, though over two thirds is received at ports on the south shore of Lake Erie

and forwarded by rail to Pittsburg, Pennsylvania. This city is the great center of the iron and steel industries. Birmingham, Alabama, is the center of the industry in the South, because near it the necessary ore, coal, and limestone are conveniently located.

### Metallurgy of Iron.

— Iron is extracted most easily from its oxides. The ores, whatever their character, are first crushed and roasted to change them into ferric oxide ( $\text{Fe}_2\text{O}_3$ ) as far as possible, and to make the raw material porous. Thus prepared, the ore is smelted with coke (or coal) and limestone in a blast furnace. The carbon reduces the oxide to metallic iron, which collects as a liquid at the bottom of the furnace beneath the slag formed by the limestone and impurities. The **blast furnace** (Fig. 72) is a huge tower, from forty to ninety feet high and from fourteen to seventeen feet in diameter at the largest part; but it is narrower at the top and bottom than in the middle.

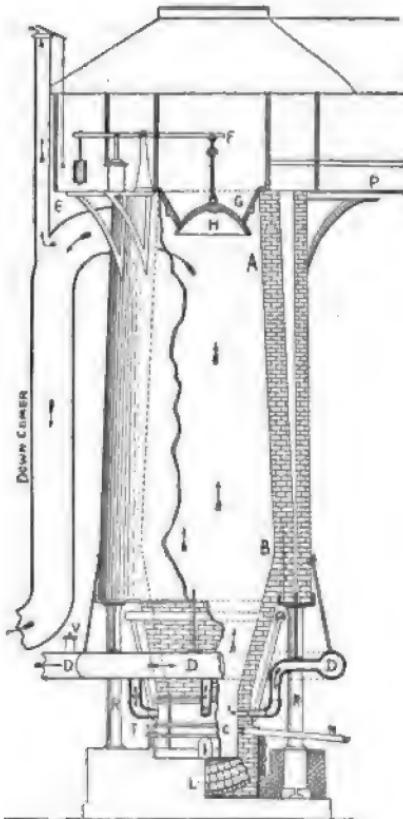


FIG. 72.—Blast furnace. *A*, throat; *B*, bosh; *C*, crucible where the melted iron collects; *D*, pipes for hot air blast; *E*, escape pipe for gases which do not escape through the "down comer"; *G*, cup; *H*, cone; *N*, trough for drawing off slag; *T*, tuyere; *I*, hole through which iron is withdrawn.

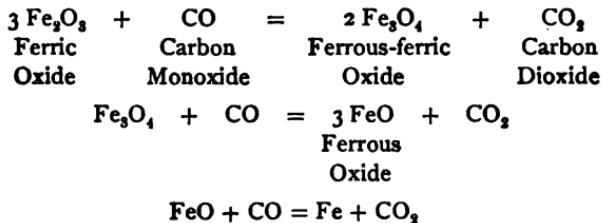
It is built of masonry and iron, and lined with fire brick. Pipes at the bottom, called **tuyeres**, allow large quantities of hot air to be forced into the furnace and up through the contents, thereby producing the high temperature required in the melting; while another pipe at the top not only permits the escape of hot gaseous products, but conducts them into a series of pipes which lead to different parts of the plant, where the hot gases are utilized as fuel. The blast pipes correspond to the bellows used by a blacksmith, and the exit pipe to a chimney, except that gases escaping through chimneys are usually wasted.

When the furnace has been heated to the proper temperature, or is already in operation, the ore, coke, limestone, etc., are carried to the top of the furnace by machinery and introduced into the furnace by dumping them upon the cone-shaped cover; their weight lowers the cover, which flies back tightly into place after the materials roll into the furnace. The charge consists of alternate layers of ore, fuel, and flux. The fuel is coke, or coke mixed with coal. The **flux** varies with the ore, but it is usually limestone, though feldspar and sand are used if the ore contains lime compounds. The object of the flux is twofold. (1) It removes the impurities from the charge in the form of a fusible glass called **slag** or cinder, and (2) thereby prevents the reduced iron from reuniting with oxygen of the air which is being constantly blown in. As the smelting proceeds, the iron falls through the slag to the bottom of the furnace, where both are drawn off through separate openings. Fresh charges of definite weight are added at regular intervals, and the whole operation continues without interruption for months or even years.

The iron from the furnace is usually poured into molds

of sand or iron and allowed to solidify. Such iron is **pig iron** or **cast iron**. A single large furnace will produce in a day about 500 tons of pig iron. In some plants the molten iron is run into huge vessels, called converters, and made directly into steel (see below).

The chemical changes involved in the metallurgy of iron are numerous and complicated. In general, the iron oxide is reduced to metallic iron largely by carbon monoxide. The carbon of the fuel at first forms carbon dioxide with the oxygen of the air blast. But the dioxide is soon reduced by the hot carbon to the monoxide, which interacts with the ore, thus —



Considerable carbon monoxide escapes, however, in the waste gas. At this stage the iron becomes porous, and is doubtless prevented from re-oxidation by the carbon dioxide liberated from the decomposed limestone. As the spongy iron sinks into the hotter part of the furnace, it combines with carbon to some extent, finally melts, sinks through the slag, and accumulates at the bottom, or hearth, of the furnace. The iron obtained in this way contains small amounts of carbon, sulphur, phosphorus, silicon, and manganese.

**Varieties of Iron.** — The iron we use and speak of is not pure iron, but largely a mixture or compound of iron with other elements, chiefly carbon. It is customary to speak of three varieties of iron, — cast iron, steel, and wrought iron. This classification is based chemically upon the per cent of carbon they contain, though their physical properties are modified by the presence of silicon,

phosphorus, sulphur, and manganese, as well as by the special method of manufacture. The different varieties are closely related, and pass easily and gradually into each other. Commercially, there are several kinds of cast iron and many kinds of steel.

**Cast Iron** is the most impure variety. It contains, besides carbon, the impurities mentioned above. It has a crystalline structure, and is brittle. The proportion of carbon varies from 3 to 5 or more per cent. If most of the carbon is combined with the iron, the metal is called **white cast iron**. But if the molten metal cools slowly, much of the carbon remains uncombined as graphite, and the color of the iron is gray; this kind is **gray cast iron**. It is softer than the white variety, and melts at a lower temperature. Although cast iron is brittle, it will withstand great pressure. It cannot be welded or forged, that is, hot pieces cannot be united, nor be shaped by hammering. But it is extensively used to make castings. This is the kind of iron used in an ordinary iron foundry. The iron, which melts at a comparatively low temperature (about  $1200^{\circ}$  C.), is heated in a furnace similar to a blast furnace, and when molten is poured into sand molds of the desired shape. Stoves, pipes, pillars, railings, parts of machines, and many other useful objects are made of cast iron. Birmingham, Alabama, is the center of the cast-iron industry in the United States.

Cast iron containing 5 to 20 per cent of manganese is called **spiegel iron**, while **ferro-manganese** contains from 20 to 85 per cent of manganese. Both are used in making steel.

**Wrought Iron** is the purest variety of commercial iron. It contains not more than 0.5 per cent of carbon and sometimes only 0.06 per cent, the average being 0.15 per cent. It is tough, malleable, and fibrous. It can be bent. Un-

like cast iron, it does not withstand pressure, but it will sustain great weight. An iron wire will sustain the weight of nearly a mile of itself. It melts at such a high temperature ( $1600^{\circ}$  to  $2000^{\circ}$  C.) that it is not used for casting. It can be forged and welded, and is therefore often called **malleable iron**. It may be seen undergoing these operations in a blacksmith's shop. It can also be rolled into plates and sheets and drawn into fine wire; in these forms the metal is very strong. Wrought iron is made into wire, sheets, rods, nails, spikes, bolts, chains, anchors, horseshoes, tires, and agricultural implements. It is less important than formerly, since it is being largely replaced by steel.

Wrought iron is made from cast iron by burning out the impurities. The process is technically called **puddling**. Cast iron is heated in a furnace, much like a reverberatory furnace, lined on the bottom and sides with iron ore (ferric oxide,  $Fe_2O_3$ ). The intense heat melts the cast iron; its carbon and silicon are removed partly by the oxygen of the air, but mainly by the oxygen of the iron oxide. As the mass becomes pasty, owing to its higher melting point, it is stirred vigorously, or "puddled." At the proper time the lumps are removed and hammered, or more often rolled between ponderous rollers. This operation removes the slag, and if the rolling is repeated, the quality of the iron is improved; the final rolling leaves the iron in the shape desired for market.

**Steel** is intermediate between cast iron and wrought iron as far as its proportion of carbon is concerned. Many grades of steel are manufactured, and their physical properties depend not only upon the presence of other elements besides carbon, especially phosphorus, silicon, and certain metals, but also upon the raw materials, the method of manufacture, and subsequent treatment.

The properties of steel are numerous. It is both fusible and malleable, and hence can be forged, welded, and cast. It is harder, stronger, and more durable than pure iron, and is more serviceable. But its most valuable property is the varying hardness which it can be made to acquire. If steel is heated very hot and then suddenly cooled by immersion in cold water or oil, it becomes brittle and very hard. But if heated and then cooled slowly, it becomes soft, tough, and elastic. All grades of hardness may be obtained between these extremes. And if the hardened steel is reheated to a definite temperature, determined by the color the metal assumes, and then properly cooled, a definite degree of hardness and elasticity is obtained. This last operation is called **tempering**. Every kind of tool has a temper determined by its use. Special grades of hard steel are also made by the addition of certain metals, especially chromium and nickel. **Harveyized steel** is made by packing steel in a mixture of charcoal and boneblack, and heating it to a very high temperature. This operation hardens the surface. This brand of steel is extensively used as armor plate in warships.

**Manufacture of Steel.** — The aim in the manufacture of steel is to prepare a product containing little or no sulphur, phosphorus, and silicon, but the *desired* proportion of carbon. This may be done by three general methods : (1) the carbon may be partly removed from cast iron, (2) carbon may be added to wrought iron, (3) cast iron may be added to wrought iron. The first method is difficult to operate, and is seldom used. The other methods are utilized by several processes.

(1) In the **cementation** or **crucible process**, wrought iron and carbon are packed in tight fire-clay boxes and heated for several days. The iron slowly absorbs carbon

in some way unknown at present, and becomes a steel of extreme purity and excellent quality. The bars are melted in graphite crucibles to make the metal of uniform quality, and cast into large bars called **ingots**. This process is long and expensive, but the steel is considered the best for fine tools.

(2) The **Bessemer process** is the one in most general use. It was introduced about 1860, and has practically revolutionized steel making. By the economical, scientific, and extensive application of this process, all grades of steel are quickly made at such a relatively small cost that the use of this metal has been enormously extended, much to the prosperity of the United States. About two thirds of the annual production is Bessemer steel. The process consists in burning out the impurities in cast iron by forcing air through the molten metal, and then adding enough iron of known composition to give the desired proportion of carbon. The operation is carried on in a converter (Fig. 73). This is a huge, egg-shaped vessel, supported so that it can be rotated into different positions; it is also provided with holes at the bottom through which a powerful blast of air can be blown. It is made of thick wrought iron plates, and is lined with an infusible mixture rich in silica. The converter is swung into a horizontal position and five to twenty tons of molten pig iron are poured in direct from the blast furnace. The air blast is turned on, and the converter is swung back to a vertical position. As the air is forced through the molten metal, the temperature rises, the carbon is oxidized to carbon



FIG. 73.—Converter.

monoxide which burns on the surface of the metal, and the silicon is oxidized to silicon dioxide, which is taken up by the slag. This oxidation generates enough heat to keep the metal melted, and no fuel need be used. As soon as the impurities have been burned out, sufficient spiegel iron is added to furnish the proper amount of carbon. By adding spiegel iron of known composition, Bessemer steel of any desired grade is produced. After the completion of the operation, which takes about twenty minutes, the contents of the converter are poured into molds.

(3) In the Bessemer process, sulphur and phosphorus are not removed. Both are objectionable impurities; sulphur makes steel brittle when hot, and phosphorus makes it brittle when cold. The **Thomas-Gilchrist process** is a modification of the Bessemer process by which the sulphur and phosphorus can be removed. The converter is lined with a mixture of lime and magnesia, called a basic lining, lime is also added to the charge of pig iron, and the blast is continued a little longer than in the Bessemer process; otherwise the operations are the same. The phosphorus forms a phosphate and the sulphur a sulphate, both of which are taken up by the lining. The lining, which is known as **Thomas slag**, is used as a source of phosphorus for fertilizers.

(4) In the **Siemens-Martin or open-hearth process**, a mixture of cast iron, scrap iron, and iron ore in the proper proportions is placed on the hearth (*H*) of an open-hearth furnace (Fig. 73 *a*) and heated several hours by a very hot gas flame obtained by forcing air and gas through hot brick checkerwork (*A, B* and *C, D*). The impurities form a slag with the hearth lining. When a test shows that the metal contains the desired proportion of carbon, ferromanganese is added, and the charge is then poured into molds.

The open-hearth process yields a tough, elastic steel, which is excellent for bridges, large machines, large guns, and gun carriages.

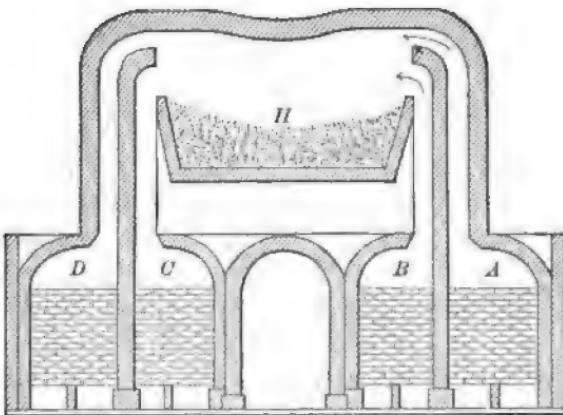
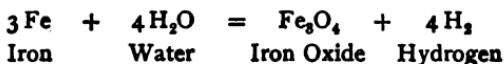


FIG. 73 a.—Open-hearth furnace.

**Properties of Iron.**—Chemically pure iron, though uncommon in commerce, may be obtained in the laboratory by reducing the oxide with hydrogen and by electrolysis. Such iron is called iron "by hydrogen," or electrolytic iron. The purest commercial form is the wrought iron used for piano wire. Pure iron is a silvery white, lustrous metal. It is softer than ordinary iron, but melts at a higher temperature. The specific gravity is about 7.8. It is attracted by a magnet, but soon loses its own magnetism. Dry air has no effect upon iron, but moist air containing carbon dioxide rusts it. Iron rust is a complex compound, but its essential constituent is a ferric hydroxide ( $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$ ). Rusting proceeds rapidly, because the film of rust is not compact enough to protect the metal. Like many metals, iron readily interacts with dilute acids, and as a rule hydrogen and ferrous compounds are the products.

With nitric acid various products result, according to the conditions,—ferrous nitrate and ammonium nitrate, if the acid is cold, but ferric nitrate and oxides of nitrogen if the acid is warm. If a clean iron wire is dipped into fuming nitric acid and then into ordinary nitric acid, no action is apparent. The iron is said to be **passive**. This peculiar fact has not been adequately explained. Steam and hot iron interact, thus—



(See Preparation of Hydrogen.)

**Compounds of Iron.**—Iron forms two series of compounds,—the ferrous and the ferric. They are analogous to cuprous and cupric, mercurous and mercuric compounds. **Ferrous compounds** in an acid solution pass into the corresponding ferric compound by the action of oxidizing agents, *e.g.* oxygen, nitric acid, potassium chlorate, potassium permanganate, and chlorine. Conversely, **ferric compounds** are reduced to the ferrous by reducing agents, *e.g.* hydrogen, hydrogen sulphide, sulphur dioxide, and stannous chloride. The passage from one series to the other occurs easily, especially from ferrous to ferric. In most of its compounds, iron acts as a metal. Many compounds of iron have industrial importance, as well as scientific interest.

**Oxides and Hydroxides of Iron.**—Iron forms three oxides. **Ferrous oxide** ( $\text{FeO}$ ) is an unstable black powder. **Ferric oxide** ( $\text{Fe}_2\text{O}_3$ ) occurs native in many varieties as hematite—the most abundant ore of iron. It may be prepared by heating ferrous sulphate or ferric hydroxide. Large quantities are obtained as a by-product in the manufacture of Nordhausen (or fuming) sulphuric acid and of galvanized iron and tinned ware. It is sold under the names rouge, crocus, and Venetian red. It is used to polish glass and jewelry, and to make red paint. **Ferrous**

ferric or ferroso-ferric oxide (magnetic oxide of iron,  $\text{Fe}_3\text{O}_4$ ) occurs native as magnetite; if noticeably magnetic, it is called **loadstone**. It is produced as a black film or scale by heating iron in the air; heaps of it are often seen beside the anvil in a blacksmith's shop. The firm coating of this oxide formed by exposing iron to steam protects the metal from further oxidation.

**Ferrous hydroxide** ( $\text{Fe}(\text{OH})_2$ ) is a white solid formed by the interaction of a ferrous salt and an alkali, such as sodium hydroxide. Exposed to the air, it soon turns green, and finally brown, owing to the formation of ferric hydroxide. **Ferric hydroxide** ( $\text{Fe}_2(\text{OH})_6$ ) is a reddish brown solid, formed by the interaction of ammonium hydroxide (or any alkali) and a ferric salt. Several ferric hydroxides are known. The freshly prepared compound is an antidote for arsenic.

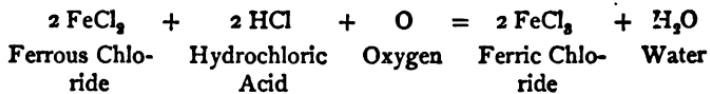
**Ferrous Sulphate** ( $\text{FeSO}_4$ ) is a green salt obtained by the interaction of iron (or ferrous sulphide) and dilute sulphuric acid, and is a by-product in several industries (e.g. see Ferric Oxide). It is prepared on a large scale by oxidizing iron pyrites ( $\text{FeS}_2$ ); this is accomplished simply by roasting, or more often by exposing heaps of pyrites to moist air. The mass is extracted with water containing scrap iron and a small proportion of sulphuric acid. From the clear solution, large light green crystals are obtained. The crystallized salt ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) is also called **green vitriol** or **copperas**. Exposed to the air, ferrous sulphate effloresces and oxidizes. Large quantities are used as a mordant and a disinfectant, and in manufacturing ink, bluing, and pigments. Much black writing **ink** is made essentially by mixing ferrous sulphate, nutgalls, gum, and water. Blue ink is usually made of Prussian blue—an iron compound (see below)—oxalic acid, and water.

**Ferric Sulphate** ( $\text{Fe}_2(\text{SO}_4)_3$ ) is formed by oxidizing an acid solution of ferrous sulphate with nitric acid. When ferric sulphate solution is

mixed with the proper quantity of potassium (or ammonium) sulphate, **iron alum** ( $K_2Fe_4(SO_4)_4 \cdot 24H_2O$ ) is formed. It is a violet, crystallized solid, which has properties like ordinary alum. Iron alum is used chiefly as a mordant.

**Iron Sulphides.** — There are two iron sulphides. Commercial **ferrous sulphide** ( $FeS$ ) is a black, brittle, metallic-looking solid, but the pure compound is yellow and crystalline. It is also obtained as a black powder by the interaction of a dissolved ferric or ferrous salt and ammonium (or potassium) sulphide. It is made on a large scale by fusing a mixture of iron and sulphur. It is used chiefly in preparing hydrogen sulphide. **Ferric sulphide** (iron disulphide, iron pyrites, pyrite,  $FeS_2$ ) is one of the commonest minerals. It is a lustrous, metallic, brass-yellow solid. Crystals of pyrites, found in many rocks, are often mistaken for gold—hence the popular name “fool’s gold.” It is valueless as an iron ore, but large quantities are used as a source of sulphur in making sulphuric acid. Over one and a half million tons are annually consumed in the acid industry. The largest pyrite producers are Spain, France, Portugal, Germany, and the United States. The domestic output comes chiefly from Virginia, Colorado, Massachusetts, and New York.

**Iron Chlorides.** — When iron interacts with hydrochloric acid, **ferrous chloride** ( $FeCl_2$ ) is formed in solution. Heated in the air, or better with potassium chlorate or nitric acid, it is changed into **ferric chloride**, thus—

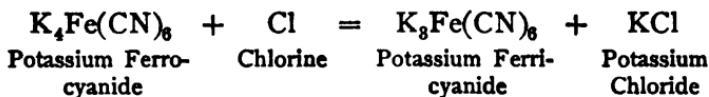


Ferric chloride is a black, lustrous, crystalline solid; but owing to its extreme deliquescence, it is usually sold as a solution, which is a dark brown liquid. It is prepared by passing chlorine into a ferrous chloride

solution, or by the interaction of iron and *aqua regia*. When treated with nascent hydrogen or another reducing agent, ferric chloride is changed into ferrous chloride.

**Ferrous Carbonate** ( $\text{FeCO}_3$ ) occurs native as the iron ore siderite, clay iron stone, or spathic iron ore. The typical variety is light yellow or brown, lustrous, crystalline, and not very hard; but many kinds are impure, and the properties vary. It is slightly soluble in water containing carbon dioxide, and is therefore found in some mineral springs (see Chalybeate Waters). Like all carbonates, it yields carbon dioxide with warm hydrochloric acid.

**Iron Cyanides.**—Iron and cyanogen ( $\text{CN}$ ), with or without potassium, form several compounds. The most important is **potassium ferrocyanide** ( $\text{K}_4\text{Fe}(\text{CN})_6$ ). It is a lemon-yellow, crystallized solid, containing three molecules of water of crystallization. Unlike most cyanogen compounds, it is not poisonous. Its commercial name is **yellow prussiate of potash**. It is manufactured by fusing together iron filings, potassium carbonate, and nitrogenous animal matter (such as horn, hair, blood, feathers, and leather). The mass is extracted with water, and the salt is separated by crystallization. In Germany this salt is manufactured from the iron oxide which has been used to purify illuminating gas. Large quantities are used in dyeing and calico printing, and in making bluing and potassium cyanogen compounds. **Potassium ferricyanide** ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) is a dark red, crystalline solid, containing no water of crystallization. It is often called **red prussiate of potash**. It is manufactured by oxidizing potassium ferrocyanide with chlorine, thus —



It is very soluble in water, forming a deep yellow, unstable solution. In alkaline solution it is a vigorous oxidizing

agent, and therefore finds extensive use in dyeing. It is also used as one of the ingredients of the sensitive coating of "blue print" paper.

Ferrous salts and potassium ferricyanide interact in solution and produce **ferrous ferricyanide** ( $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ ). This is a blue solid and is often called Turnbull's blue. But ferrous salts produce with potassium ferrocyanide a white precipitate (ferrous ferrocyanide), which quickly oxidizes to a complex blue compound. Ferric salts interact with potassium ferrocyanide and produce **ferric ferrocyanide** ( $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ ). This is a dark blue solid, and is called Prussian blue or Berlin blue. Ferric salts produce no precipitate with potassium ferricyanide. Prussian blue is extensively used in dyeing and calico printing, and in making bluing. The above reactions, which allow ferrous and ferric salts to be distinguished, may be summarized as follows : —

CYANIDE.	FERROUS SALT.	FERRIC SALT.
Ferrocyanide	Whitish precipitate	Prussian blue
Ferricyanide	Turnbull's blue	No precipitate

Besides the above tests, potassium sulphocyanate produces a dark red liquid with ferric salts, but leaves ferrous salts unchanged. The tests for iron are thus numerous and specific.

#### NICKEL.

**Nickel**, Ni, occurs combined with arsenic, sulphur, or both. Small amounts of metallic nickel are found in meteorites. The chief ores are nickel-bearing iron sulphides, which are abundant in the Sudbury district, Canada, and the silicates found in New Caledonia. A small amount is produced in the United States as a by-product in smelting lead ores from a Missouri mine.

**Nickel is obtained from its Ores** by complicated processes, and is now refined by electrolysis. It is a white

metal, which takes a brilliant polish. It is ductile, hard, tenacious, and does not tarnish in the air. Like cobalt, it is attracted by a magnet.

**Nickel has varied Uses.** — For many years it has been used as one ingredient of the small coins of several countries. The per cent of nickel varies from 12 in the United States cent to 25 in the five-cent piece. German silver contains from 15 to 25 per cent of nickel, the rest being copper and zinc. Large quantities of nickel are used to coat or plate other metals, especially iron and brass. The **nickel plating** is done by electrolysis, as in the case of silver and gold plating, though the electrolytic solution used is a sulphate of nickel and ammonium, not a cyanide. The deposit of nickel is hard, brilliant, and durable. Nickel becomes malleable, if a little magnesium is added to the molten metal, and sheets of iron covered with such nickel are made into vessels for cooking. **Nickeloid** is a nickel-plated sheet zinc. Its attractive appearance and non-corrosive property adapt it for the manufacture of reflectors, refrigerator linings, bath tubs, show cases, and signs. The most important use of nickel is in the manufacture of **nickel steel** which contains varying proportions of nickel. Large quantities are used for the armor plates and turrets of battleships, and for parts of machinery requiring great strength.

Nickel forms two series of compounds, — the nickelous and the nickelic. The nickelous are more common, and many of them are green. The **test for nickel** is the formation of the apple-green hydroxide ( $\text{Ni(OH)}_2$ ) by the interaction of an alkali and the solution of a nickel salt.

**Cobalt, Co,** generally occurs combined with arsenic and sulphur, and is often associated with nickel compounds. It is a lustrous metal with a reddish tinge, harder than iron, but less magnetic. The hydrated

compounds are red in solution, anhydrous compounds are blue. Hence red crystallized salts turn blue when heated. Some cobalt compounds are used to color glass, porcelain, and paper, especially a cobalt silicate. This is known as smalt, or smalt blue; and since it is unchanged by sunlight, acids, or alkalies, it is used to decorate porcelain. Other pigments are cobalt blue (an oxide of cobalt and aluminium), and Rinmann's green (an oxide of cobalt and zinc). The blue color produced by fusing cobalt compounds into a borax bead is the test for cobalt.

#### EXERCISES.

1. What is the symbol of iron? From what word is it derived?
2. Discuss the occurrence of iron. Name the chief ores. Name other compounds of iron. What proportion of the earth's crust is iron?
3. Discuss (*a*) the production and transportation of iron ore in the United States, and (*b*) the production of iron.
4. What is the general chemical change in the metallurgy of iron? Describe a blast furnace. Summarize the smelting of iron. Discuss the chief physical and chemical changes involved in the smelting.
5. Name the varieties of iron. How do they differ essentially? What is (*a*) galvanized iron, (*b*) meteoric iron?
6. Describe cast iron. State its composition, properties, and uses.
7. Describe the manufacture of wrought iron. State its composition, properties, and uses.
8. State the composition and properties of steel. Compare briefly with cast and wrought iron. What is tempering?
9. Describe the manufacture of steel by the following processes: (*a*) cementation, (*b*) Bessemer, (*c*) Thomas-Gilchrist, (*d*) Siemens-Martin.
10. State the uses of steel.
11. State the properties of iron.
12. How are ferrous changed into ferric compounds, and *vice versa*?
13. How is ferric oxide prepared? What is the native form called? For what is crocus used?
14. What is the formula and chemical name of magnetic oxide of iron? What is loadstone? How is magnetic oxide of iron produced? What is the native form called?
15. Describe ferric hydroxide. What is its use?
16. Describe ferrous sulphate. How is it prepared? For what is it used? What is copperas?

17. What is iron alum? How is it related to ordinary alum?
18. Describe ferrous sulphide. How is it made? For what is it used? Compare it with ferric sulphide. Discuss the occurrence and use of the latter.
19. Describe ferrous carbonate.
20. Describe potassium ferrocyanide. How is it made? State its properties and uses. What is its common name? Its formula?
21. Describe potassium ferricyanide. For what is it used? How is it related chemically to potassium ferrocyanide?
22. Describe the tests for iron. What is Prussian blue? For what is it used?
23. Discuss the occurrence of nickel. State its properties and uses. Describe nickel plating. What is (a) a "nickel," (b) nickel steel? What is the test for nickel?
24. State the properties of cobalt. For what are its compounds used? What is smalt? What is the test for cobalt?

#### **PROBLEMS.**

1. Calculate the percentage composition of (a) ferric oxide, (b) ferrous sulphate, (c) ferrous sulphide ( $\text{FeS}$ ).
2. If 1.586 gm. of iron form 2.265 gm. of ferric oxide, what is the atomic weight of iron? (Equation is  $2 \text{Fe} + 3 \text{O} = \text{Fe}_2\text{O}_3$ .)

## CHAPTER XXIX.

### PLATINUM AND ASSOCIATED METALS.

**Occurrence of Platinum.**—Platinum occurs as the essential ingredient of platinum ore or so-called native platinum. The ore contains from 60 to 86 per cent of platinum. The other metals present are ruthenium, osmium, iridium, rhodium, and palladium. Iron, gold, and copper are also usually present. Only one native compound is known, viz. platinum arsenide (*sperrylite*,  $\text{PtAs}_2$ ).

The ore is found chiefly in the Ural Mountains in Russia, but some comes from South America, Australia, and Borneo. The United States produced about 1440 ounces of metallic platinum in 1906, but the usual amount is very much less. It came from the gold deposits in California and the copper mines in Wyoming. The latter source also furnished osmium, palladium, and iridium. The world's annual production of metallic platinum for the last few years has been about 200,000 ounces. Russia supplies over 90 per cent of this amount.

The word *platinum* is derived from *platina*, a form of the Spanish word *plata*, meaning silver, because native platinum was regarded as an impure ore of silver by the Spaniards, who first discovered it in South America about 1735. Platinum is now sometimes called by its old name *platina*.

**Preparation of Platinum.**—The platinum ore, which occurs in rounded grains or flattened scales, is first digested with dilute *aqua regia* to remove the gold, silver, and copper; and then with concentrated *aqua regia*, which changes all the platinum and a very little iridium into soluble compounds, leaving behind an alloy of iridium and osmium. From the clear solution the platinum and iridium are precipitated by ammonium chloride as compounds, which, on heating, yield the metals as a spongy mass. This spongy platinum is melted in a

lime crucible with an oxhydrogen flame, or hammered while hot into **sheet platinum**. The very small amount of iridium is seldom removed from the metallic platinum.

**Properties and Uses of Platinum.** — Platinum is a lustrous, grayish white metal. It is malleable and ductile, and usually appears in commerce in the form of wire and sheets. Sheet platinum is cut into squares—the familiar platinum foil of the laboratory, or made into crucibles, dishes, and stills for sulphuric and hydrofluoric acid (Fig. 74). Its use in these forms is due partly to its infusibility and partly to its resistance to acids and other corrosive chemicals. Although it is attacked by fused caustic alkalies and a few other substances, it is practically indispensable in the chemical laboratory. Platinum is a good conductor of elec-



FIG. 74.—A platinum dish.

tricity, and large quantities are consumed in incandescent electric light bulbs. Short pieces of wire are fused into the glass at the base of the bulb and attached to the outside wires, conveying the current to and from the carbon filament within. Platinum is the only metal thus far found which is perfectly adapted to this use. Dentists use alloys of platinum as a filling for teeth, and some is made into jewelry. The demand exceeds the supply, and in the last five years the price of this rare metal has doubled, reaching \$38 an ounce in 1906. Platinum has a specific gravity of about 21, which is higher than that of any known substance, except osmium and iridium. In the form of a black, porous mass it is called **spongy platinum**,

and a still finer form is called **platinum black**. Both forms absorb large volumes of gases; and if a current of the gas is directed against the metal, the gas often takes fire. Metallic platinum has the same property to a less degree, for it becomes red-hot if held in a stream of illuminating gas, and often ignites the gas. Palladium has similar properties (see Occlusion). Platinum forms alloys with other metals, and should never be heated with lead, similar metals, or their compounds, since the alloys have a low melting point. With iridium, however, it forms a very hard alloy of which the international metric apparatus is made.

**Platinic Chloride** ( $\text{PtCl}_4$ ) is the only important compound of platinum. It is a brownish solid formed by treating platinum with *aqua regia* and evaporating the solution to dryness. The solution is used in chemical analysis, and in photography to produce "platinum prints." **Chloroplatinic acid** ( $\text{H}_2\text{PtCl}_6$ ) forms complex salts, of which the yellow, crystalline **potassium chlorplatinate** ( $\text{K}_2\text{PtCl}_6$ ) and **ammonium chlorplatinate** ( $(\text{NH}_4)_2\text{PtCl}_6$ ) are the best known.

The Metals associated with **Platinum** have limited uses. **Palladium** is used in chemical analysis to absorb hydrogen, **osmium** is utilized in the Auer incandescent electric light, and a native (as well as an artificial) alloy of **iridium** and osmium, called **iridosmine**, is used to tip gold pens.

#### **EXERCISES.**

1. Name the metals related to platinum.
2. Discuss the occurrence of platinum.
3. What is (a) native platinum, (b) spongy platinum, (c) platinum black, (d) platinum foil, (e) sheet platinum?
4. Discuss the production of platinum.
5. What is the symbol of platinum? What is the derivation of the word *platinum*?
6. Describe the preparation of platinum. Summarize its properties. State its uses.
7. Describe platinic chloride.
8. State the uses of the metals related to platinum.

PROBLEMS.

1. A piece of platinum foil measuring 10.5 cm. by 1.5 cm. weighs 0.723 gm. Into how many pieces, each weighing 1 dg., may it be divided?
2. The specific heat of platinum is 0.0324. According to analysis, 35.5 gm. of chlorine unite with 48.6 gm. of platinum to form platinic chloride. What is (*a*) the atomic weight of platinum, and (*b*) the formula of platinic chloride?

## CHAPTER XXX.

### GENERAL RELATIONS OF THE ELEMENTS.

**Introduction.**—In the preceding chapters emphasis has been laid on individual elements. Certain group relations were also pointed out, but little or nothing was said concerning the elements as a single large group. The elements are not independent. They possess certain fundamental properties, which show that although apparently very different, they are really closely related. In this chapter we shall consider two topics which illustrate this general fundamental relationship, viz. the periodic law and spectrum analysis.

#### THE PERIODIC LAW.

**Classification of the Elements.**—As the number of elements increased, attempts were made to classify them. About the time of Lavoisier (1743-1794) they were roughly divided into metals and non-metals. Those elements were called metals which were hard, lustrous, heavy, and good conductors of heat, while the others were called non-metals. This classification proved to be misleading as additional elements were discovered. It is used, however, even now, because many common elements fall readily into one of these classes.

Classification according to acid and basic properties prevailed for a time. But it was abandoned largely because such a basis of division excluded elements exhibiting

both acid and basic properties, such as arsenic, antimony, chromium, and aluminium.

The elements have also been classified according to their **valence** into six or seven groups (the mono-, di-, tri-, etc.). But this plan has been largely given up on account of so many troublesome cases of variable and unsatisfied valence (see Valence).

About 1828 Dumas pointed out striking resemblances between certain elements, and he suggested several **groups** or **families**. For example:—

(1)	(2)	(3)	(4)
Lithium	Selenium	Calcium	Nitrogen
Sodium	Sulphur	Strontium	Phosphorus
Potassium	Oxygen	Barium	Arsenic

This classification was arbitrarily based on selected physical and chemical properties. It was interesting but incomplete, because it emphasized resemblances and overlooked differences—that is, the basis of comparison was not broad enough.

The first actual progress began to be made about 1850, when chemists became deeply interested in the significance of atomic weights. Dumas (in 1857) and others pointed out certain remarkable **numerical relations** existing between the atomic weights of related elements. Thus, the atomic weight of sodium is half the sum of the atomic weights of lithium and potassium —

$$\text{Li} = 7, \text{Na} = 23, \text{K} = 39. \quad \frac{7 + 39}{2} = 23.$$

The same is true of phosphorus, arsenic, and antimony —

$$\text{P} = 31, \text{As} = 75, \text{Sb} = 120. \quad \frac{31 + 120}{2} = 75.5.$$

The existence of other relations similar to these, together with a deep desire to obtain more accurate atomic weights and a growing interest in the properties of the elements themselves, focused the attention of chemists at this time (1855-1865) upon the **relation of properties to atomic weights**. Several things fostered the above principle. One was the atomic weight determinations of Stas, whose masterly work proved beyond doubt that Prout was incorrect when he insisted in 1815 that the atomic weights are whole numbers. Another was the acceptance by most chemists of the same table of atomic weights. A third was the rapid accumulation of many facts about the elements and their compounds. Chemists were ready for a new classification of the elements.

**The Periodic Classification.** — Previous to 1869 no classification included all the elements. In that year the Russian chemist Mendeleeff published a **classification of the elements according to the periodic law**. His views had been partially anticipated by several chemists, and were soon amplified by the German chemist, Lothar Meyer. Their classification of the elements revealed a new relation between the properties of the elements and their atomic weights. If all the elements are arranged in the order of their increasing atomic weights beginning with helium, their properties will vary periodically, *i.e.* at certain regular intervals or periods elements will be found which have similar properties. In other words, a certain increase in atomic weight causes a reappearance or return of properties. The general relation is often summarized in the **Periodic Law** —

*The properties of the elements are periodic functions of their atomic weights.*

# General Relations of the Elements.

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## PERIODIC CLASSIFICATION OF THE ELEMENTS

Periods.	Group O.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
1		H = 1.008							
2	He = 4	Li = 7.00	Be = 9.1	B = 11.0	C = 12.0	N = 14.01	O = 16.00	F = 19.0	
3	Ne = 20.0	Na = 23.00	Mg = 24.32	Al = 27.1	Si = 28.3	P = 31.0	S = 32.07	Cl = 35.46	
4	A = 39.9	K = 39.10	Ca = 40.09	Sc = 44.1	Ti = 48.1	V = 51.2	Cr = 52.1	Mn = 54.93	Fe = 55.85 Ni = 58.68 Co = 58.97
5		Cu = 63.57	Zn = 65.37	Ga = 69.9	Ge = 72.5	As = 75.0	Se = 79.2	Br = 79.92	
6	Kr = 81.8	Rb = 85.45	Sr = 87.62	Y = 89.0	Zr = 90.6	Cb = 93.5	Mo = 96.0		Ru = 101.7 Rh = 102.9 Pd = 106.7
7		Ag = 107.88	Cd = 112.40	In = 114.8	Sn = 119.0	Sb = 120.2	Te = 127.5	I = 136.92	
8	Xe = 128.0	Cs = 132.81	Ba = 137.37	La = 139.0	Ce - Yb <sup>1</sup> 140 - 173	Ta = 181.0	W = 184.0		Os = 190.9 Ir = 193.1 Pt = 195.0
9		Au = 197.2	Hg = 200.0	Tl = 204.0	Pb = 207.10	Bi = 208.0			
10				Ra = 226.4	Th = 232.42	U = 238.5			

<sup>1</sup>This set includes several elements more or less doubtful or still under investigation.

Function here means the exhibition of some special relation, viz. that of properties to atomic weight. Interpreted freely, the law means (1) properties and atomic weight are related, they depend upon each other; and (2) this relation is exhibited again and again as we reach elements with increasing atomic weights at regular intervals in the successive arrangement.

The Periodic Table originally proposed by Mendeleeff has been modified from time to time, as new facts have necessitated. The table generally accepted at the present time is given on page 399.

From the table it is seen that the elements fall naturally into two subdivisions. (1) Those in the same vertical column belong to the same natural group or family. Thus, in Group I are found the alkali metals, in Group II the alkaline earth metals, in Group VII the halogens. (2) The elements in the same horizontal row belong to the same period. The periodic variation of their properties is illustrated by periods 2 and 3 (omitting Group 0). Beginning with lithium, the general chemical properties vary regularly with increasing atomic weight. Thus, the metallic character gradually diminishes until fluorine is passed and sodium is reached; here it reappears. Proceeding onward from sodium, the same gradation of properties is noticed until potassium is reached, and here again the marked metallic character in the same way reappears. There is no sudden change in properties until we pass from one period to the next. Thus, fluorine at the end of the second period forms a powerful acid, but sodium at the beginning of the third period forms a strong base. Similarly, chlorine is strongly acidic; but potassium, which begins the next period, is markedly basic; chlorine is a typical non-metal, while potassium is a typical metal. Not

all elements fit the periodic classification equally well, but the arrangement is at least very suggestive, and doubtless expresses an approximately truthful relation.

The Gaps in the Periodic Classification probably correspond to elements not yet discovered. Three such gaps, which were in the original table, have been filled. When Mendeleeff proposed his arrangement, he predicted the discovery of three elements having definite properties. These elements,—gallium, scandium, and germanium,—have since been discovered and now occupy their predicted place in the table. Possibly other gaps will be filled by newly discovered elements.

The discovery of the predicted elements was not the only immediate service of Mendeleeff's table. It also emphasized the necessity of more accurate atomic weights. Several elements did not fall into their proper places, and careful investigation showed that their accepted atomic weights were incorrect. Thus, the atomic weights of beryllium and indium were changed to their present values, and the present order of the platinum metals was adopted; iodine and tellurium are still being studied. The position of argon, helium, etc., and certain metals is still doubtful owing to a limited knowledge of their properties and atomic weights. Hydrogen, also, still lacks a place.

#### SPECTRUM ANALYSIS.

**Introduction.**—When light from an ordinary gas flame, glowing lime or other solid, or a Welsbach flame is passed through a prism and falls upon a white surface, a long band of color is produced. The colors are perfectly blended, and are arranged like the familiar colors of the rainbow. This band of colors is called a **spectrum**. The white light has been separated or analyzed into the colored. The examination and study of the spectrum of a substance is spectrum analysis, and it is accomplished by a spectroscope.

The Spectroscope consists essentially of a prism and tubes, one of which is a telescope (Fig. 75). The light enters a slit in the tube, passes



FIG. 75.—A spectroscope.

through, and falls upon the prism. Here it is bent from its path, and as it emerges from the prism, it may be viewed through the telescope as a magnified spectrum.

**Kinds of Spectra.**—(1) The spectrum of an incandescent solid is a **continuous band** of colors. (2) But the spectra of gases are narrow, colored, vertical bars or lines, separated by black spaces. Thus, sodium vapor has a yellow line, potassium a red and a violet line, and barium several lines where the green and yellow parts of the ordinary spectrum occur. Each element which is a gas, or which can be vaporized, has its own **bright line spectrum**. The lines always occupy the same relative positions, which in most cases have been very carefully determined. Therefore, when examined through a spectroscope, the yellow line of sodium will always be seen in its proper place, and the red and violet potassium lines in their places. Therefore, by examining the light from different substances, it is possi-

ble to tell what elements they contain. (3) The spectrum of sunlight is the familiar band of colors, but it is crossed vertically by many black lines, which have fixed positions (Fig. 76). It is believed that the sun is a glowing hot solid, surrounded by very hot gases. It therefore should

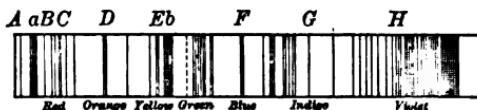


FIG. 76.—Spectrum of sunlight showing some of the vertical lines.

give the two kinds of spectra,—the continuous and the bright line. Now it has been proved that the vapor of an element absorbs the light given out by the same element when solid. Hence the dark lines which appear in the solar spectrum are caused by the absorptive power of the gases in the sun's atmosphere. The solar spectrum is often called an **absorption spectrum**.

**Spectrum Analysis.**—In the laboratory the spectroscope is used to detect the presence of certain elements, more especially the metals. If the metal or one of its compounds is put on a platinum wire and held in the Bunsen flame before the slit, the characteristic spectrum of the element can be easily recognized in the telescope. Two spectra do not interfere, because each line has its own place. Hence several elements may be distinguished in a mixture. Minute quantities are easily detected by the spectroscope. Rare elements, which can be obtained only in very small quantities or with great difficulty, are studied by the spectroscope. Thus, Bunsen, who (with Kirchhoff) devised the improved spectroscope, discovered the rare metals, rubidium and cæsium. And within the last few years the spectroscope has been especially serviceable

in studying argon, helium, krypton, neon, and xenon. By means of the spectroscope it has been shown that the sun contains many elements found in our earth. According to a reliable authority, about thirty of the elements known to us are present in the sun. The spectroscope also enables astronomers to tell the nature of stars, comets, nebulæ, and other heavenly bodies. The stars thus far examined give spectra crossed by dark lines, and therefore these bodies are like the sun; but nebulæ give bright line spectra, and hence consist of incandescent gases.

#### EXERCISES.

1. Discuss the classification of the elements according to (a) metals and non-metals, (b) acid and basic properties, (c) valence, (d) groups based on resemblances, (e) numerical relations.
2. What is the fundamental idea of the periodic classification? How does it differ from previous systems? When and by whom was this classification proposed and developed?
3. State the periodic law. Explain it. What is meant by (a) function, (b) period, (c) group?
4. Illustrate the law by (a) the alkali metals, and (b) the halogens.
5. Discuss the gaps in the periodic arrangement of the elements.
6. Of what use has this law been?
7. State some objections to it.
8. Describe (a) a continuous spectrum, (b) a line spectrum, (c) an absorption spectrum.
9. Describe a spectroscope. How is it used?
10. What kind of a spectrum is produced by (a) a glowing solid, (b) a glowing vapor, (c) a glowing solid surrounded by a glowing vapor?
11. What is spectrum analysis? How is it applied (a) in the laboratory, and (b) by astronomers?
12. What does spectrum analysis show about each element? About their relations to each other? About their distribution? About the heavenly bodies?
13. Who perfected the spectroscope and developed its use?
14. What recent use has been made of the spectroscope in (a) chemistry, and (b) astronomy?

## CHAPTER XXXI.

### SOME COMMON ORGANIC COMPOUNDS.

**Introduction.** — In the early days of chemistry it was believed that starch, sugar, and other compounds obtained from plants and animals were produced by the influence of some mysterious vital force. Such compounds were called **organic**, because of their connection with living things, *i.e.* with bodies having organs; and they were sharply distinguished from **inorganic** or mineral compounds obtained from the earth's crust. This distinction prevailed until Wöhler, in 1828, prepared urea — a characteristic organic compound — from inorganic substances. Since then the barrier between the two classes of compounds has been completely removed. We now believe that compounds of carbon, whatever their source, are subject to the laws that govern all other compounds. The terms *organic* and *inorganic* are still used, though they have lost their original narrow meaning. Carbon forms a vast number of compounds which are related to each other, and which differ markedly from most compounds of other elements. It is convenient, therefore, to distinguish these compounds by the term **organic** and to study them under the comprehensive title of **Organic Chemistry** or the Chemistry of Carbon Compounds.

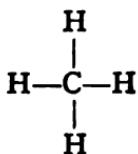
**Composition of Organic Compounds.** — The number of organic compounds is very large, but they contain only a few elements — seldom more than four or five. Hydro-

carbons, as already indicated, contain carbon and hydrogen. Vegetable substances, typified by starch, sugar, and fruit acids, contain carbon, hydrogen, and oxygen. Animal substances, like hair, albumen, gelatine, and muscle generally contain nitrogen as well as carbon, hydrogen, and oxygen; some also contain sulphur or phosphorus. Artificial organic compounds, like dyestuffs, may contain any element, especially chlorine, iodine, and metals.

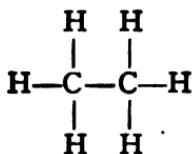
The number and complexity of organic compounds is due to several facts already mentioned in a previous chapter. (1) Atoms of carbon have power to unite with themselves. (2) Atoms of different elements can be introduced into carbon compounds. Sometimes these atoms are simply added, sometimes they replace other atoms, thus producing an endless number of addition and substitution products. (3) The same number of atoms may arrange themselves differently, thereby producing isomeric compounds having different properties. To these principles, which should be reviewed until firmly grasped, must be added another. (4) Organic compounds contain radicals. These **radicals** are analogous to hydroxyl ( $\text{OH}$ ) and ammonium ( $\text{NH}_4$ ), and like these radicals they exist only in combination. They act like single atoms and enter unchanged into a number of organic compounds. The radical  $\text{C}_2\text{H}_5$  is called **ethyl**. It is present in many organic compounds, and its presence in ordinary alcohol gives rise to the scientific name, *ethyl alcohol*. **Methyl** ( $\text{CH}_3$ ) is another important radical, and **phenyl** ( $\text{C}_6\text{H}_5$ ) is especially common in the benzene series of organic compounds.

**Structure of Organic Compounds.** — An extensive study of the properties of organic compounds has revealed many facts about their **constitution**, *i.e.* the structure of their

molecules. Little or nothing, of course, is known about the shape, size, etc., of molecules, but much is known about the grouping of atoms and of radicals in the molecules. These facts, which are ascertained by experiment and are often too complex to be expressed briefly, may be represented by suitable formulas. The ordinary or **empirical formula** of alcohol is  $C_2H_6O$ . But this formula tells nothing about the relation these atoms bear to each other, nor whether all the hydrogen atoms act alike. Experiment proves, however, that (1) one hydrogen atom acts differently from the other five, and (2) one hydrogen atom is always associated with the oxygen atom in chemical changes. Hence, the formula  $C_2H_6 \cdot OH$  expresses more fully these facts. Such a formula is called a **rational** or **constitutional formula**. Sometimes constitution is expressed by a **graphic formula**. Thus methane and ethane have the graphic formulas —



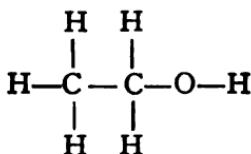
Methane



Ethane

In these diagrams the single lines represent a valence of one — nothing else, and the number of lines connected with each atom must be equal to the valence of the element in the compound. The lines are sometimes called bonds or links, but they are not intended to represent attraction or any other force. Nor do they represent space relations. In the case of methane, they mean that the four hydrogen atoms bear the same relation to the single carbon atom. In the case of ethane, they mean the same,

but they also indicate that the two carbon atoms are joined. The graphic formula of ethyl alcohol is—



This is not an arbitrary arrangement; the facts mentioned above necessitate this general arrangement. Additional illustrations of this subject will be given, as different compounds are discussed.

**Classification of Organic Compounds.**—Organic compounds are divided and subdivided into many classes for purposes of study. Only the most common organic compounds can be considered in this book. These are members of the following groups: (1) Hydrocarbons, (2) Alcohols, (3) Aldehydes, (4) Ethers, (5) Acids, (6) Ethe-real salts, (7) Fats, glycerine, and soap, (8) Carbohydrates, (9) Benzene and its derivatives. Some compounds are so closely related that they really belong to several of these groups, while a few cannot strictly be put in any of them.

#### HYDROCARBONS.

Three of these compounds of carbon and hydrogen have been fully considered in Chapter XV. The chief facts and fundamental principles recorded there may be profitably reviewed at this point. Other hydrocarbons will be discussed under Benzene (see below).

#### ALCOHOLS.

**Alcohols** are compounds of carbon, hydrogen, and oxygen. Ordinary or ethyl alcohol is the best known member

of this group. It is usually called simply alcohol. There are many alcohols analogous to ethyl alcohol, but the only other important one is methyl alcohol.

The alcohols may be regarded as hydroxides of certain radicals, *e.g.* ethyl, methyl, propyl, etc.<sup>1</sup> For example, ethyl alcohol is ethyl hydroxide, and may be considered as formed by replacing one hydrogen atom of ethane ( $C_2H_6$ ) by one hydroxyl group (OH). Again, alcohols are analogous to metallic hydroxides, in which the metal is replaced by a radical, thus—



Alcohols and metallic hydroxides have some properties in common. Thus, both form salts with acids. With acetic acid, sodium hydroxide forms sodium acetate, while alcohol forms ethyl acetate (see Ethereal Salts).

**Methyl Alcohol**,  $CH_3 \cdot OH$ , is a colorless or slightly yellowish liquid, much like ordinary alcohol. It boils at about  $66^{\circ} C.$ , and burns with a pale flame which deposits no soot. It intoxicates, and if concentrated is poisonous. It mixes with water in all proportions. It is cheaper than ethyl alcohol, and is used as a solvent for fats, oils, and shellac, and in the manufacture of varnishes and dyestuffs. Methyl alcohol is often called **wood alcohol** or **wood spirit**, because it is one of the liquid products obtained by the dry distillation of wood (see Charcoal).

**Ethyl Alcohol**,  $C_2H_5 \cdot OH$ , is a colorless, volatile liquid, having a burning taste and a pleasant odor. It is lighter than water, its specific gravity being about 0.8. It boils at  $78.3^{\circ} C.$ , and does not freeze until at  $-130.5^{\circ} C.$  Because of its very low freezing point, it is used in ther-

<sup>1</sup> The names of these and similar radicals are derived from the corresponding hydrocarbon. Thus, the word *methyl* comes from *methane*, *ethyl* from *ethane*, *propyl* from *propane*.

mometers designed to record temperatures below  $-40^{\circ}$  C. (the freezing point of mercury), as in polar explorations. Its harmful effect on the human system need not be discussed. Alcohol mixes with water in all proportions. The ordinary commercial variety contains from 50 to 95 per cent of alcohol. Pure or **absolute alcohol** is obtained by removing the remaining water with lime. **Proof spirit** contains about 50 per cent of alcohol. **Denatured alcohol** is a mixture of 100 parts ethyl alcohol, 10 parts methyl alcohol, and a small proportion of benzine, or pyridine (or a similar mixture); it is not taxed, and in its legalized forms is used as a cheap substitute for ordinary alcohol. Alcohol is an excellent solvent for gums, oils, and resins, and is therefore extensively used in the manufacture of varnishes, essences, extracts, tinctures, perfumes, and medicines. It is also used as an antiseptic, and as a source of heat in alcohol lamps. Many organic compounds, as ether and chloroform, are prepared from alcohol. Some vinegar is made from alcohol. In museums alcohol is used to preserve specimens. Alcohol may be prepared from ethane (see below), but it is manufactured by the fermentation of sugars.

**Fermentation** is a general term for the chemical changes caused by **ferments**. The latter are usually minute living

bodies, and they secrete complex compounds which are called **enzymes**. The process and essential products vary with the nature of the ferment. The important kinds of fermentation are alcoholic, acetic, and lactic, and the respective products are alcohol, acetic acid, and lactic acid. **Alcoholic fermentation** is caused by an enzyme from yeast. Under the microscope, yeast looks like slimy yellow chains of small, round cells (Fig. 77). When yeast is added to a solution



FIG. 77.  
Yeast cells.

of glucose, or any other fermentable sugar, the yeast plants multiply rapidly. Air must be admitted, and the temperature should be 20°–30° C. The changes are numerous and complex, but the main products are alcohol and carbon dioxide, thus —



The fermentation ceases as soon as the liquid contains about 14 per cent of alcohol. The solution is filtered and concentrated by distillation, until the distillate contains the desired per cent of alcohol. Commercial alcohol is made also from potatoes, grains, rice, beet root, molasses, and many other substances rich in sugar and starch. Ordinary or cane sugar must be boiled with acid before it will ferment.

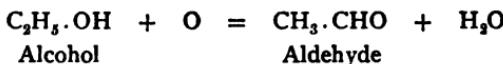
**Wines, beers, and all alcoholic liquors are prepared by fermentation.** Yeast is seldom added, however, because the ferment which brings about the change is in the air, upon fruits and vines. Wines are made from the juice of grapes; beer is made from hops and malt (barley which has sprouted). Whisky, gin, brandy, rum, and cordials are called **distilled liquors**, and are manufactured by distilling the liquid obtained by fermenting grains, molasses, fruit juices, and other substances containing sugar and starches. Hence, wine, beer, and similar liquors are essentially mixtures of alcohol and water. They differ mainly in their proportion of alcohol. The particular flavor is due to small quantities of different substances which are intentionally added, obtained from the raw materials, or formed by special processes of manufacture. Coloring matter is usually added, but sometimes it is extracted from the casks in which the liquor is stored. Beer contains from 3 to 7

per cent of alcohol, wines from 6 to 20, rum, brandy, and whisky from 40 to 60 or more per cent.

#### **ALDEHYDES.**

**Aldehydes** are compounds of carbon, hydrogen, and oxygen. They are formed by the oxidation of alcohols. The two important members of this group are acetic aldehyde (or acetaldehyde) and formic aldehyde (or formaldehyde).

**Acetic Aldehyde**,  $\text{CH}_3 \cdot \text{CHO}$ , is usually called simply aldehyde. It is a colorless, very volatile liquid, and has a peculiar, suffocating odor. It is a vigorous reducing agent, and is sometimes used to precipitate silver, as a thin coating, from silver solutions: It is converted by oxidizing agents into acetic acid (hence its name, *acetic aldehyde*). Aldehyde is prepared by oxidizing alcohol with a solution of potassium (or sodium) dichromate and sulphuric acid. When a mixture of these three substances is gently warmed, the characteristic odor of aldehyde may be detected. The oxidation of alcohol consists simply in the removal of hydrogen, thus —

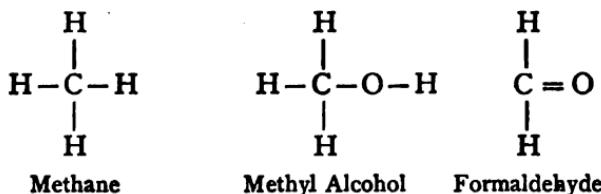


The word *aldehyde* emphasizes this fact, being a contraction of *alcohol dehydrogenatum*.

When chlorine is used to oxidize alcohol, part of the hydrogen is replaced by chlorine, and the compound  $\text{CCl}_3 \cdot \text{CHO}$  is formed. This substance, called **chloral**, forms a **hydrate** ( $\text{CCl}_3 \cdot \text{CHO} \cdot \text{H}_2\text{O}$ ), which is used to induce sleep and relieve pain. When chloral is treated with an alkali, it is decomposed and **chloroform** ( $\text{CHCl}_3$ ) is produced. The latter is a sweet liquid, and is used to produce insensibility in surgical operations. Chloroform is usually made by treating alcohol with bleaching powder. **Iodoform** ( $\text{CHI}_3$ ), which is analogous to chloroform, is a yellow solid, with a disagreeable smell, and is extensively used as a dressing for wounds. It protects the wound from the harmful action of germs.

**Formaldehyde**,  $\text{H} \cdot \text{CHO}$ , is a gas, but is used only in solution. It has a penetrating odor. The commercial solu-

tion sold as **formalin** contains 40 per cent of formaldehyde. It corresponds to methane and methyl alcohol, thus —



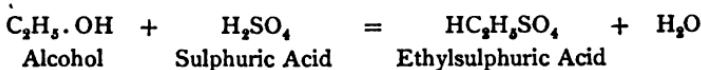
With oxygen it forms formic acid (hence its name, see below). Large quantities of formaldehyde are used in the manufacture of dyestuffs and fuming nitric acid, as a food preservative, and a disinfectant. When used for the last purpose, the solution is vaporized in a special apparatus, and the vapors are conducted by a small tube into the room to be disinfected. It is one of the most convenient and efficient of all disinfectants, and is very generally used.

#### ETHERS.

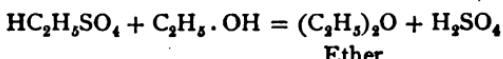
**Ethers** are compounds of carbon, hydrogen, and oxygen. They are analogous to the metallic oxides. They are formed by heating alcohols with sulphuric acid. Ordinary or ethyl ether is the best known member of this group.

**Ethyl Ether**,  $\text{C}_2\text{H}_5\text{O}$ , is a colorless, volatile liquid, with a peculiar, pleasing taste and odor. It is lighter than water, its specific gravity being about 0.74. It boils at  $35^\circ \text{ C.}$ , and the vapor is very inflammable. The liquid should never be brought near a flame. It is somewhat soluble in water, and it also dissolves water to a slight extent. It mixes with alcohol in all proportions. It is a good solvent for waxes, fats, oils, and other organic compounds. Its chief use is as an anæsthetic, *i.e.* to render one insensible to pain in surgical operations.

Ether is manufactured by distilling a mixture of ethyl alcohol and sulphuric acid in the proper proportions. Hence, the names, — *ethyl* or *sulphuric ether*. Ethylsulphuric acid is first produced, thus —



When more alcohol and the ethylsulphuric acid are heated together, ether is formed, and sulphuric acid is reproduced, thus, —

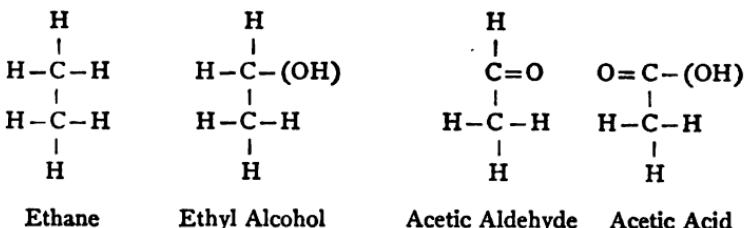


The process is thus continuous, a small quantity of sulphuric acid serving to transform a large quantity of alcohol into ether. Ethyl ether is ethyl oxide,  $(\text{C}_2\text{H}_5)_2\text{O}$  or  $\text{C}_2\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5$ .

#### ACIDS.

**Organic Acids** are compounds of carbon, hydrogen, and oxygen. It is a large class of compounds divided into several series, one of the most important of which is the **acetic or fatty series**. Its best known member is acetic acid; several of the higher members occur in fats and oils.

These acids are closely related to hydrocarbons, alcohols, and aldehydes, as may be seen by the following formulas : —



It is thus possible to pass from a hydrocarbon through a corresponding alcohol and aldehyde to an acid.

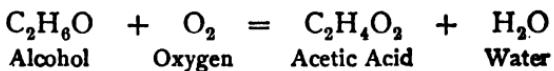
The characteristic group of atoms in organic acids is  $\text{COOH}$  (or  $\text{O}=\text{C}-\text{O}-\text{H}$ ), and is called carboxyl.

**Acetic Acid**,  $C_2H_4O_2$  or  $CH_3.COOH$ . — This is the most common organic acid. It is manufactured on a large scale by the dry distillation of wood. The dark red watery distillate, which is called **pyroligneous acid**, contains about 10 per cent of acetic acid besides a small per cent of methyl alcohol and many other organic compounds. This distillate is neutralized with lime or sodium carbonate, and the acetate formed is then decomposed and distilled with hydrochloric or sulphuric acid. The acetic acid which condenses in the receiver may be further purified by distilling it with potassium dichromate and then filtering through charcoal. Sometimes the pyroligneous acid is distilled without neutralizing; the distillate is then dilute, impure acetic acid, known as **wood vinegar**. If sodium acetate, prepared as described above, is fused and then distilled with concentrated sulphuric acid, the product is a very concentrated acetic acid. It is called **glacial acetic acid**, because at about  $17^{\circ} C.$  it becomes an icelike solid.

Commercial acetic acid is a water solution containing about 30 per cent of pure acetic acid. It is a colorless liquid, having a pleasant odor and a sharp taste. It is slightly heavier than water. It mixes with water and alcohol in all proportions, and like alcohol is an excellent solvent for many organic substances. Recently, it has begun to replace alcohol as a solvent for many drugs.

Acetic acid is used to prepare acetates, dyestuffs and other organic compounds, medicines, white lead, and in the manufacture of vinegar.

**Vinegar** is dilute, impure acetic acid. It is prepared by oxidizing dilute alcohol, the essential change being represented thus —



The transformation is accomplished by fermentation. Two processes are used. (1) When beer, weak wines, or cider are exposed to the air, they slowly become sour, owing to the conversion of alcohol into acetic acid. The change is caused by the presence and activity of a ferment, known as *mycoderma aceti*, or "mother of vinegar." Strong wines and pure dilute alcohol do not become sour, because the ferment cannot live in such liquids. (2) In the "quick vinegar process," impure dilute alcohol is oxidized by exposing it to an excess of air. The operation is conducted

in tall vats or casks filled with beechwood shavings soaked in strong vinegar (Fig. 78). Holes at the bottom and top allow air to enter and escape freely. The alcoholic solution is introduced at the top, trickles through the shavings, and collects at the bottom. In its passage it comes in contact with the ferment and oxygen, and is partially converted into vinegar. The operation is repeated until



FIG. 78.—Apparatus for the preparation of vinegar from impure, dilute alcohol.

the change is complete. Thus prepared, the vinegar lacks the flavor, odor, and color of cider vinegar, but these deficiencies are often artificially supplied.

Vinegar is used chiefly as a condiment for the table and in making pickles and similar relishes.

The constitution of acetic acid has been shown to correspond to the formula  $\text{CH}_3 \cdot \text{COOH}$ . Its metallic salts are formed by substituting a metallic atom (or group) for the hydrogen of the group  $\text{COOH}$ . The radical  $\text{CH}_3$  remains unchanged. (See page 170.)

**Acetates.**—Acetic acid is a monobasic acid, and forms a series of salts—the acetates. They are prepared like other salts by the interaction of the acid and carbonates, hydroxides, metals, etc. The metallic acetates are usually crystallized solids, which readily yield acetic acid when treated with sulphuric or a similar acid. Most of them contain water of crystallization, and most are poisonous.

Several acetates have useful applications. **Sodium acetate**,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ , is a white crystallized solid, used in preparing pure acetic acid, and in the manufacture of dyestuffs. **Lead acetate**,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , is a white crystallized solid, used in dyeing and in making a yellow pigment. Its sweet taste led to the common name of "sugar of lead." **Aluminium acetate**,  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ , is not known in the pure state, but an impure solution, known as "red liquor," is extensively used in dyeing and calico printing. **Iron acetates** are sold in solution as a complex black liquid, known as "iron liquor," which is used in dyeing black silks and cottons, and in calico printing (see Mordants). A complex copper acetate,  $2\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{CuO}$ , called **verdigris**, is used in making blue paint. Another complex acetate of copper and arsenic is **Paris green**; it is used to kill potato bugs and other insects which injure vegetation.

A few other acids in this series are interesting. **Butyric acid**,  $\text{C}_4\text{H}_8\text{O}_2$ , is the acid which gives the disagreeable odor to rancid butter. **Stearic acid**,  $\text{C}_{18}\text{H}_{36}\text{O}_2$ , and **Palmitic acid**,  $\text{C}_{16}\text{H}_{32}\text{O}_2$ , are found as compounds in beef suet, mutton fat, butter, and other fats. Palmitic acid is also one of the essential compounds found in palm oil. These two acids are white solids, and are used to make stearin candles (see Fats, below).

Other Organic Acids which are important are oxalic, lactic, malic, tartaric, and citric.

**Oxalic Acid** occurs as a salt in rhubarb and sorrel. It is manufactured on a large scale by heating sawdust with potassium hydroxide, and treating the residue first with lime and then with sulphuric acid. Oxalic acid is a white solid, very soluble in water, from which it crystallizes with

two molecules of water of crystallization ( $C_2H_2O_4 \cdot 2 H_2O$ ). It is very poisonous. It is dibasic and forms several useful salts. The acid and some of its salts decompose iron rust and inks containing iron, and are often used to remove such stains from cloth. The acid and its salts are also used in dyeing, calico printing, photography, in making dyestuffs, and as an ingredient of mixtures for cleaning brass and copper.

**Lactic Acid**,  $C_3H_6O_3$ , occurs in sour milk, being one product of the fermentation of the milk sugar. It is a thick, sour liquid, and is easily decomposed by heat. When sour milk is used in cooking, the "baking soda" and lactic acid interact, producing soluble sodium lactate and carbon dioxide gas. Lactic acid and its salts are used as medicines, in beverages, and as a substitute for more expensive acids in dyeing and calico printing.

**Malic acid**,  $C_4H_6O_5$ , is found free and as salts in apples, pears, currants, gooseberries, rhubarb, grapes, and berries of the mountain ash tree. It is a white, crystalline solid.

**Tartaric Acid**,  $C_4H_6O_6$ , occurs as the potassium salt in grapes and other fruits. During the fermentation of grape juice, impure acid potassium tartrate is deposited in the casks. From this **argol** or crude **tartar** the acid itself is prepared by treating the raw product successively with chalk and sulphuric acid. Tartaric acid is a white crystallized solid, soluble in water and alcohol. It is used in dyeing, and as one ingredient of Seidlitz powders. In these and similar powders it serves to decompose the other ingredient which is a carbonate (see Sodium Bicarbonate).

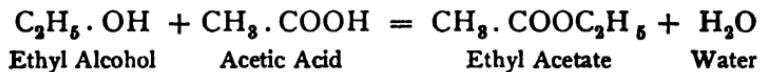
Tartaric acid is dibasic and forms two classes of salts. Purified acid potassium tartrate obtained from argol is commonly known as **cream of tartar**. It is extensively used in the manufacture of baking powders. These, as a rule, are essentially mixtures of cream of tartar

and sodium bicarbonate,  $\text{HNaCO}_3$ . When moistened by dough, the baking powder dissolves, the two ingredients interact and liberate carbon dioxide as the main product. This gas bubbles slowly through the dough, thereby puffing it up and making it porous (see Sodium Bicarbonate). **Tartar emetic** is a tartrate of potassium and antimony. It is used as a medicine and to some extent in dyeing.

**Citric Acid**,  $\text{C}_6\text{H}_8\text{O}_7$ , occurs abundantly in lemons and oranges, and in small quantities in currants, gooseberries, and raspberries. It is a white, crystallized solid, very soluble in water. The taste is sour, but pleasant. The acid and its magnesium salt are used as medicines. The acid itself is used in calico printing. Citric acid is tribasic.

#### ETHERAL SALTS.

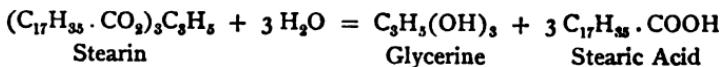
**Ethereal Salts or Esters** are compounds of carbon, hydrogen, and oxygen closely related to alcohols and organic acids. Thus, when ethyl alcohol, acetic acid, and concentrated sulphuric acid are mixed and warmed, **ethyl acetate** is formed. The essential change is represented thus—



The sulphuric acid serves to absorb the water. Ethyl acetate has a pleasant, fruitlike odor, and its formation in this way is a simple test for alcohol or acetic acid. Ethyl acetate is analogous to sodium acetate, *i.e.* the organic salt contains the radical ethyl while the metallic salt contains sodium. The fatty acids, as well as those of other series, form many ethereal salts of special interest. Some occur naturally in fruits and flowers, and in many cases give the flavor and fragrance. Others are prepared artificially and used as the basis of cheap flavoring extracts, perfumery, and beverages. Ethyl butyrate has the taste and fragrance of pineapples, amyl acetate of bananas, amyl valerate of apples.

## FATS, GLYCERINE, AND SOAP.

**General Relations.** — Natural fats and oils are essentially mixtures of stearin, palmitin, and olein. Beef and mutton fat are chiefly stearin, lard is mainly palmitin and olein ; while oils, such as olive oil, are largely olein. Stearin and palmitin are solids at the ordinary temperature, but olein is a liquid. These three compounds — stearin, palmitin, and olein — are ethereal salts of their corresponding acids and the alcohol, glycerine. They are analogous to ethyl acetate. The radical of glycerine is glyceryl,  $C_3H_6$ . Thus, **stearin** is glyceryl stearate, **palmitin** is glyceryl palmitate, and **olein** is glyceryl oleate. Natural fats and oils, therefore, are mixtures of these and similar ethereal salts. Fats are sometimes called glycerides. **Glycerine** is a triacid alcohol containing three hydroxyl ( $OH$ ) groups. Like ordinary alcohol, it interacts with the fatty acids and forms ethereal salts. The latter, as we have just learned, are the fats. Now when fats are heated with very hot steam or with sulphuric acid, the fats themselves are changed into glycerine and the corresponding acids. Thus, with stearin, the change is —



But if fats are boiled with sodium hydroxide or a similar alkali, glycerine and an alkaline salt of the corresponding acid are formed. **Soap** is a mixture of such alkaline salts. In a few words, the general relations are these : (1) fats are ethereal salts. (2) Treated with steam or acid, fats form glycerine and fatty acids. (3) Treated with alkalies, fats form glycerine and soap.

**Natural Fats and Oils** are often complicated mixtures. The solid fats, as already stated, are rich in stearin and

palmitin. **Tallow** is chiefly stearin, but human fat and palm oil are largely palmitin. The soft and liquid fats and oils contain considerable olein, as a rule. The proportion of olein determines the consistency of the fats and oils. Thus, **olive oil** contains about 72 per cent of olein (and a similar fat) and 28 per cent of stearin and palmitin. The specific character of many fats and oils is due mainly to the presence of a small proportion of certain fats. These fats correspond to uncommon acids in the fatty, oleic, and other series. **Butter**, for example, consists mainly of the fats corresponding to the following acids: palmitic, stearic, oleic, butyric, capric, and caproic. The last three with traces of other substances give butter its pleasant flavor. **Oleomargarine** and other substitutes for butter resemble real butter very closely in composition. Artificial butter, however, lacks the flavor of the real butter, but it is "probably just as nutritious, although perhaps not quite so easily digested." The lack of flavor noticed in artificial butter is due to the absence of the fats corresponding to the acids of low molecular weight. **Cottolene** is a mixture of beef fat and cotton-seed oil; it is used as a substitute for lard.

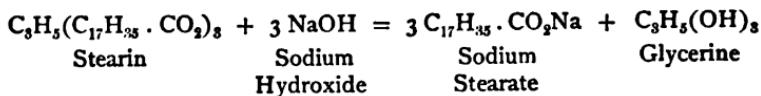
**Glycerine** ( $C_3H_8O_3$  or  $C_3H_5 \cdot (OH)_3$ ) is a thick, sweet liquid. It mixes readily with water and with alcohol in all proportions, and absorbs moisture from the air. Heated in the air, it decomposes and gives off irritating gases, like those produced by burning fat.

Glycerine is used to make nitroglycerine (see below), toilet soaps, printers' ink rolls; it is also used as a solvent, a lubricator, a preservative for tobacco and certain foods, a sweetening substance in certain liquors, preserves, and candy; as a cosmetic; and, owing to its non-volatile and non-drying properties, it is used as an ingredient of inks and oils.

Glycerine is a by-product in the manufacture of soap, or it is made directly by decomposing fats with steam under pressure or with lime. All these methods involve the chemical change described above, viz. the decomposition of an ethereal salt (the fat) into the corresponding alcohol (glycerine) and a mixture of fatty acids. By skillful treatment the glycerine is freed from water and impurities. The mixture of fatty acids is made into the so-called "stearin" candles.

As already stated, glycerine is an alcohol, and for this reason it is often called glycerol. When treated with a mixture of concentrated nitric and sulphuric acids, it forms an ethereal salt commonly known as nitroglycerine ( $C_3H_5(ONO_2)_3$ ). This is a yellow, heavy, oily liquid. It is the well-known explosive, and is also an ingredient of some other explosives. When kindled by a flame, it burns without explosion; but if struck by a hammer or heated suddenly by a percussion cap, it explodes violently. Nitroglycerine is used in blasting; but since it is dangerous to handle and transport, it is usually mixed with some porous substance, such as infusorial earth, fine sand, or even sawdust. In this form it is called dynamite.

**Soap**, as already stated, is a mixture of alkaline salts of organic acids, mainly stearic and palmitic acids. Soap is made by boiling fats with sodium hydroxide or potassium hydroxide. This process is called **saponification**. Sodium hydroxide produces hard soap, consisting chiefly of sodium palmitate, sodium stearate, and sodium oleate. Potassium hydroxide produces soft soap, which is mainly the corresponding potassium salts. The chemical change, as already stated, consists in the transformation of an ethereal salt (fat) into glycerine and an alkaline salt. In the case of pure stearin (glyceryl stearate) the change may be represented thus —



The fats used in **soap making** vary with the soap. Tallow, lard, palm oil, and cocoanut oil make white soaps.

Bone grease or house grease, together with tallow, palm oil, cotton-seed oil, and rosin, make yellow soaps. Olive oil is used for making castile soap.

In the **cold process** the calculated amounts of alkali and fat are allowed to interact, first in a large tank and then in a box called a "frame." By this process the glycerine and excess of alkali are left in the soap. Most soaps are made by the **boiling process**. The fat and alkali are boiled in a huge kettle. This operation produces a thick, frothy mixture of soap, glycerine, and alkali. At the proper time, salt is added, thereby causing the soap to separate and rise to the top. The liquid beneath is drawn off, and from it glycerine is extracted. The soap is often boiled again with rosin or cocoanut oil; then purified by washing, mixed, if desired, with perfume, coloring matter, or some filling material (such as sodium silicate, sand, borax), cooled in "frames," cut, and dried. Most soaps contain water. This really assists their cleansing action. The latter is believed to be due to the free alkali formed by the decomposition of the soap when dissolved.

#### CARBOHYDRATES.

**Carbohydrates** are compounds of carbon, hydrogen, and oxygen. This is a large group, and the most important members are the sugars, starches, and cellulose.

The term *carbohydrate* is applied to these compounds because they contain hydrogen and oxygen in the proportion to form water. They were once regarded as hydrates of carbon, or carbon hydrates — a view which is incorrect and misleading.

**Sugars.** — The popular term *sugar* means almost any sweet substance found in fruits, nuts, vegetables, sap of trees, etc., though it is usually restricted to the ordinary white sugar obtained from sugar cane and sugar beet. Chemically, there are many sugars, each having a definite constitution. The most important is ordinary sugar, which is also called **cane sugar, sucrose, and saccharose**. Another important sugar is **glucose**.

**Cane Sugar**,  $C_{12}H_{22}O_{11}$ , is widely distributed in nature, being found in the sugar cane, sugar beet, sugar maple, Indian corn, sorghum, most sweet fruits, many nuts, blossoms of flowers, and honey. The main source of cane sugar is the sugar cane and sugar beet.

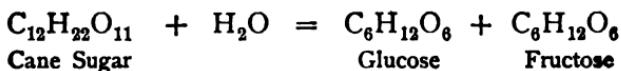
Saccharose, or ordinary sugar, is a white, crystallized solid. Rock candy is highly crystallized sugar. It is soluble in water, but only sparingly soluble in alcohol. Heated to  $160^{\circ}\text{ C.}$ , sugar melts, and on cooling forms a pale yellow colored mass, called **barley sugar**. Heated to about  $200^{\circ}\text{ C.}$ , it is changed into water and a brown mass, called **caramel**, which is used to color liquors, soups, etc. If sugar is heated with sulphuric acid, it is changed into a black mass, which is mainly carbon; several gases are also produced, such as steam, carbon dioxide, and sulphur dioxide. Cane sugar does not ferment.

The manufacture of **Cane Sugar** from sugar cane and sugar beets involves two main operations: (1) the preparation of raw sugar and (2) its purification or refining. (1) In the preparation of raw sugar from sugar cane the juice is **extracted** from the cane by crushing the latter between heavy iron rollers. The liquid is then **clarified** as soon as possible by boiling it with a little lime, removing the scum which contains much of the impurity, and finally filtering the liquid through bags or a filter press. The purified juice is next **evaporated** until the cane sugar begins to crystallize from the cooled liquid. Formerly the evaporation was accomplished in an open pan, and is now in some localities, but usually a vacuum kettle is used. The crystals are next **separated** from the liquid by allowing the latter to drip out, or more commonly by whirling it out in a centrifugal machine. The solid product is called **muscovado, raw or brown sugar**. The thick liquid is the familiar **molasses**. There are several grades of each product. The preparation of raw sugar from sugar beets resembles the method used for sugar cane. The washed beets are reduced to a pulp, or cut into slices, and then treated with water. The sugar dissolves in the water. The solution is clarified, evaporated, and separated by processes much like those applied to cane-sugar solutions. The raw sugar

can scarcely be distinguished from cane sugar. The molasses is unfit for table use, though considerable sugar is extracted from it by means of strontium hydroxide (see Strontium Hydroxide). (2) Raw sugar is usually dark colored, and must be refined before it is suitable for most uses. The **refining of sugar** consists in (a) purification, and (b) recrystallization. (a) The raw sugar is purified by first dissolving it in huge tanks. Air is blown in to agitate the heated solution, blood and other substances are often added to entangle the impurities, and lime is also added to precipitate and gather the impurities into a scum or clot. The colored liquid is next filtered, first through cloth bags and then through animal charcoal, from which it drips as a perfectly clear liquid. (b) The filtered sirup is now evaporated in a large vacuum kettle. When a sample shows that the evaporation has reached the proper point, the liquid is run into tanks to crystallize. The crystals of sugar are separated from the sirup by centrifugal machines. The latter is boiled again or sold as sirup for the table. The crystals are dried in a heated tube called a granulator, so that each grain will be separate. Hence the name **granulated sugar**. The grains are sifted and packed in barrels for the market.

**Lactose**, or sugar of milk, has the same formula as cane sugar, but its constitution and properties differ. It is obtained from milk. Its crystals are white, hard, gritty, less sweet than cane sugar; they contain one molecule of water of crystallization. Sugar of milk is used in making homeopathic pills and certain kinds of foods for infants.

**Glucose** is the name of a sugar and of a commercial mixture of glucose and several related substances. Glucose (dextrose or grape sugar,  $C_6H_{12}O_6$ ) is found in many sweet fruits, especially in grapes. Old raisins are sometimes coated with this sugar. It is often associated with **levulose** (fructose or fruit sugar)—an isomeric compound ( $C_6H_{12}O_6$ ). The two sugars are found, for example, in **honey** and in parts of some plants. Both sugars are formed from cane sugar by boiling it with a dilute acid. The chemical change may be represented thus—



Both glucose and fructose ferment, forming alcohol and carbon dioxide (see Alcohol).

The commercial mixture called "glucose" is prepared on a large scale by boiling starch with a dilute acid, usually sulphuric acid. The consistency and composition of the product vary with the details of manufacture. The liquid products are called "glucose" or "mixing sirup," while the solid product is known as "grape sugar" or "dextrose." All contain more or less glucose and are about three fifths as sweet as sugar. But since they dissolve in water, and are cheaper than cane sugar, they are used extensively in the manufacture of candy, jelly, table sirups, etc. They are also added to wines and liquors, certain medicines, and many thick liquids in which their presence is harmless. In alkaline solutions, glucose is a strong reducing agent, and is used as such in dyeing with indigo. It also reduces an alkaline mixture of copper sulphate, known as Fehling's solution. When this solution is boiled with glucose, a reddish copper compound (cuprous oxide) is formed. The presence of sugar in solution is often shown in this way.

**Starch** is widely distributed in the vegetable kingdom. It is found in wheat, corn, and all other grains, in potatoes, beans, peas, and similar vegetables, and in large quantities in rice, sago, tapioca, and nuts. Many parts of plants contain starch, for example, the stalk, stem, leaves, root, seed, and fruit. The food value of vegetables depends largely upon the starch they contain.



FIG. 79.—Starch grains (magnified)—wheat (left), rice (center), corn (right).

Starch is a white powder, as usually seen. But under the microscope it is found to consist of a mass of oval

grains, varying somewhat with the source (Fig. 79). Starch is only very slightly soluble in water. But if heated with water, the grains swell and burst, partially dissolve, and form a solution which, when cold, becomes the familiar **starch paste**. Starch in solution is turned blue by iodine, and its presence in many vegetables and foods may be readily shown by grinding the substance in a mortar with warm water and adding a drop of iodine solution.

Starch is prepared on a large scale chiefly from corn and potatoes. The operation is mainly mechanical, and consists in separating the starch from the fatty, nitrogenous, and mineral matters in the raw product. Immense quantities are consumed as food, in laundries, in finishing cloth and paper, in making glucose, and as a paste.

The composition of starch, according to some authorities, corresponds to the formula  $(C_6H_{10}O_5)_n$ , but its formula is still being investigated.

**Dextrin** is a sticky solid formed from starch by heating it to  $200^{\circ}$ - $250^{\circ}$  C. or by treating it with dilute acids. It is soluble in water and forms a sticky solution. Commercial dextrin or British gum is a mixture of dextrin and similar compounds. Mucilage contains dextrin. Large quantities are used as the gum for the backs of postage stamps, and for sticking the colors to the cloth in calico printing.

Dextrin is sometimes regarded as an intermediate product between starch and dextrose. Its composition, according to some authorities, corresponds to the formula  $C_{12}H_{20}O_{10}$ , but the statement made about the composition of starch also applies to dextrin.

**Bread.**—Wheat flour contains about 70 per cent of starch. The remainder is chiefly water and gluten in nearly equal proportions, though small quantities of mineral matter, dextrin, and other fermentable substances are present. In making bread, flour, milk or water, and a little yeast are thoroughly mixed into dough, which is put in a warm place to rise. Fermentation begins at once. The yeast changes the ferment-

able substances into alcohol and carbon dioxide. The gases, in trying to escape, puff up the dough, which literally rises and becomes light and porous. When the dough is baked, the heat kills the yeast, and fermentation stops; but the alcohol, carbon dioxide, and some water escape and puff up the mass still more. The heat, however, soon hardens the starch, gluten, etc., into a firm but porous loaf.

**Cellulose** ( $C_6H_{10}O_5$ )<sub>n</sub> is widely distributed in the vegetable kingdom. The framework of all vegetables is cellulose. It is thus analogous to the bones of animals. Wood, cotton, linen, and paper are largely cellulose. Pure cellulose is a white substance, insoluble in most liquids, but soluble in a mixture of ammonia and copper oxide. Concentrated sulphuric acid dissolves it slowly; and if the solution is diluted and boiled, the cellulose is changed into a mixture of glucose and dextrin. By this operation, wood could be made into a sugar and then into alcohol; but the method would be too expensive to use on a large scale.

Sulphuric acid of a certain strength, if quickly and properly applied to paper, changes it into a tougher form called **parchment paper**. The latter is often substituted for animal parchment (*e.g.* sheepskin), and has a variety of uses.

Cellulose has properties resembling those of alcohol. Thus it interacts with acids and forms ethereal salts. With nitric acid it forms cellulose nitrates, just as glycerine forms glycerine nitrates (see Nitroglycerine). The cellulose nitrates are the basis of **smokeless gunpowders**. One of the cellulose nitrates is **gun cotton**. It looks like ordinary cotton, and may be spun, woven, and pressed into cakes. It burns with a large flame if unconfined; but when ignited by a percussion cap or when burned in a confined space, gun cotton explodes violently. It is used in blasting. Other cellulose nitrates are known. Their solution in a mixture of alcohol and ether is called **collodion**. When poured or brushed upon a glass plate or the skin, the solvent evaporates, leaving behind a thin film. It is used in preparing certain photographic material and as a coating for wounds. The "new skin" liquid recently offered for sale is mainly collodion. It protects wounds from dusty, impure air, and thereby facilitates the healing. A mixture of camphor and cellulose ni-

trates is called **celluloid**. It is easily molded into various shapes. The white celluloid is made into collar buttons, and the colored varieties are made into toilet articles and ornaments. Celluloid smells of camphor, can be lighted with a match, and burns freely with a smoky flame.

**Paper** is chiefly cellulose. Formerly it was made from various kinds of rags; but now it is made almost entirely from wood, especially the paper used for newspapers and cheap books. The best paper, such as writing paper, is still made from linen rags.

In making paper from wood, the latter is reduced to a pulp, which is washed, spread on a frame or an endless wire gauze, dried, and pressed. The pulp is prepared by two processes, the mechanical and the chemical. **Mechanical pulp** is made by holding a stick of wood against revolving stone upon which water constantly falls. **Chemical pulp** is made by heating chipped wood with caustic soda, or with calcium acid sulphite (usually called bisulphite). The operation is conducted under pressure in huge tanks called digesters. Chemical pulp has longer and stronger fibers than mechanical pulp. The two kinds of pulp are often mixed. Most paper is loaded,—that is, clay, gypsum, or other mineral matter is mixed with the pulp to give the paper body. Paper intended for printing or writing is *sized*,—that is, the surface is coated with gelatine, rosin, or a similar substance to prevent the ink from spreading. Many kinds are also smoothed by passing them between heavy rollers. Blotting and tissue papers are not sized or loaded.

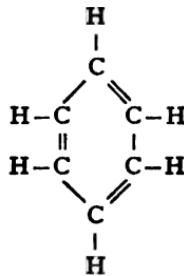
#### BENZENE AND ITS DERIVATIVES.

**Introduction.**—The hydrocarbon **benzene** was mentioned in Chapter XV as the first member of an homologous series. In the same chapter **coal tar** was described as a black, complex liquid obtained as a by-product in the manufacture of illuminating gas. Now, coal tar is the chief source of benzene and some of its related compounds, while from benzene itself hundreds of derivatives have been prepared. Some are absolutely indispensable to man, but many have

as yet merely scientific interest. Only the most important benzene compounds can be described in this book.

**Benzene**,  $C_6H_6$ , is a colorless liquid, lighter than water, and has an odor suggesting coal gas. It burns with a luminous, smoky flame, owing to its richness in carbon. Ordinary illuminating gas owes its luminosity partly to benzene. It dissolves fats, resins, iodine, sulphur, and rubber. Benzene is sometimes called **benzol**. It should not be confused with **benzine**, which is a mixture of hydrocarbons derived from petroleum. Benzene is chiefly used in preparing its derivatives.

The Constitution of Benzene has been carefully studied. For reasons too extended to state here, it is believed that in a molecule of benzene the carbon atoms are arranged in a ring. The structural formula is often written thus —



Benzene forms many derivatives. In all of them the six carbon atoms remain as a nucleus. No carbon atom can be removed from the benzene molecule without producing complete decomposition. But for the six hydrogen atoms, other atoms or radicals can be substituted. Hence, the almost infinite number of derivatives of benzene.

**Toluene**,  $C_6H_5 \cdot CH_3$ , is the second member of the benzene series. It may be regarded as methyl benzene; or as phenyl methane, that is, methane ( $CH_4$ ) in which one hydrogen atom is replaced by the radical phenyl ( $C_6H_5$ ). Toluene is obtained from coal tar, and resembles benzene in its properties.

**Nitrobenzene**,  $C_6H_5 \cdot NO_2$ , is a yellow liquid formed by the interaction of benzene and nitric acid. It is volatile, and has the odor of

bitter almonds. Although poisonous, it is used to produce the flavor of almonds in essences and perfumery. It is chiefly used, however, in the manufacture of aniline.

**Aniline**,  $C_6H_5 \cdot NH_2$ , is an oily liquid, slightly heavier than water. It is prepared on a large scale by reducing nitrobenzene with nascent hydrogen. From aniline are made many compounds known as **aniline dyes**. The starting point of these dyes is rosaniline, which is prepared by oxidizing a mixture of aniline and toluidine ( $C_6H_4 \cdot CH_3 \cdot NH_2$ ). Derivatives of rosaniline produce exceedingly brilliant colors in every variety of shade. Vast dyeing industries have risen since the value of coal tar was discovered (about 1860).

**Phenol**,  $C_6H_5 \cdot OH$ , is a white crystalline solid. It has a smoky odor, is poisonous, and burns the skin. Coal tar is the source of phenol. A solution of phenol in water, popularly called **carbolic acid**, is used as a disinfectant.

**Derivatives of Phenol** are important. **Picric acid**, or trinitrophenol ( $C_6H_2(NO_2)_3OH$ ), is a yellow crystalline solid used in dyeing silk yellow. Salts of picric acid—the picrates—are used in making explosives. Related to phenol are **hydroquinone** ( $C_6H_4(OH)_2$ ) and **pyrogallic acid** ( $C_6H_3(OH)_3$ ), which are used extensively as developers in photography.

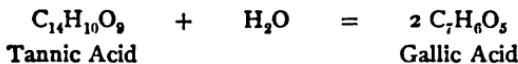
**Acids, Aldehydes, and Ethereal Salts of the Benzene Series.**—The simplest acid is **benzoic acid** ( $C_6H_5 \cdot COOH$ ). It occurs in certain balsams and gums. It is usually prepared from gum benzoin, and is a white crystalline solid with a fragrant odor. The corresponding aldehyde (benzoic aldehyde,  $C_6H_5 \cdot COH$ ) is commonly called **oil of bitter almonds**. It is a fragrant liquid and is used to some extent as a flavoring substance. **Salicylic acid** ( $C_6H_4 \cdot OH \cdot COOH$ ) is a white crystalline solid, which is extensively used as a food preservative. Sodium salicylate

is a common remedy for rheumatism. The corresponding aldehyde gives the fragrance to the wild flower known as meadowsweet; and methyl salicylate is the essential ingredient of the checkerberry.

**Naphthalene**,  $C_{10}H_8$ , is a white, lustrous, crystalline solid obtained from coal tar. It has a penetrating, unpleasant odor, and is used as a substitute for camphor under the name of "moth balls." Large quantities of naphthalene are used in making dyestuffs.

**Anthracene**,  $C_{14}H_{10}$ , is a white crystallized solid, and, like naphthalene, is obtained from coal tar. It is one of the most important hydrocarbons, because from it alizarin is made. **Alizarin** is a valuable dyestuff, not only because it produces brilliant colors with different mordants, but also because most of these colors are fast, that is, they do not fade like many aniline colors. The Turkey red so common on cotton goods, is produced by alizarin. Alizarin was formerly obtained from madder root, but now vast quantities are artificially prepared.

**Glucosides** are substances occurring in many plants and vegetables. By the action of ferment they are changed into glucose and other substances that are benzene derivatives. **Amygdalin**, for example, is found in bitter almonds, cherry and peach kernels, and laurel leaves. The ferment emulsin, which also occurs in the plants, breaks up the amygdalin into oil of bitter almonds, hydrocyanic acid, and glucose. **Tannin** is also a glucoside. The tannins are a group of related compounds found in the leaves, bark, and other parts of the oak, hemlock, and pine trees, in sumach, gallnuts, tea, coffee, and numerous plants. Several acids have been obtained from tannins. The best known are **gallic acid** and **tannic acid**; the latter is also often called simply tannin, and probably all tannins contain some tannic acid. Tannic acid changes into gallic acid according to the following equation —



## Some Common Organic Compounds. 433

The formula of gallic acid may be written  $C_6H_3(OH)_3 \cdot COOH$ , thus showing its relation to benzene. Tannin, in whatever form, produces black compounds with iron salts. Its presence in tea, hemlock bark, etc., may be shown by the formation of a black precipitate upon the addition of ferrous sulphate. This property is utilized in making writing **ink**, though some kinds of ink are now made from aniline dyes. The tannin in oak and hemlock barks is used in **tanning** leather. When raw hides are soaked in solutions of tannin, the tannic acid changes certain substances in the skin into insoluble compounds, which remain in the hide, thereby converting it into the soft pliable form known as **leather**. Tannins are also used as mordants in dyeing silk, cotton, and linen.

**Alkaloids** are complex compounds obtained from plants and vegetables. The chief property is the power to produce marked physiological effects upon animals. All of them contain nitrogen, and resemble ammonia in having an alkaline reaction and in uniting directly with acids to form salts. Their commercial form is usually a salt. Many are used as medicines and drugs, although they are poisonous, especially if taken in large quantities. **Theine** or **caffeine** is the alkaloid obtained from tea and coffee. **Nicotine** comes from tobacco and is very poisonous. **Cocaine** is obtained from the coca plant. One of its salts is used by surgeons and dentists to relieve pain. **Quinine** and **cinchonine** are extracted from the bark of the cinchona tree; both are used as a remedy for fevers. **Morphine** is the chief alkaloid found in opium. The latter is the dried sap obtained from a certain part of the unripe poppy. Morphine in different forms is used to relieve pain and induce sleep. The two familiar medicines, laudanum and paregoric, contain preparations of opium. Large doses of any form of opium may be fatal.

### **EXERCISES:**

1. How were organic and inorganic compounds once defined? Do they differ fundamentally? What compounds are now included by the term *organic*?
2. What is the essential element in organic compounds? What other elements are often present?
3. Give four reasons for the vast number of organic compounds.
4. Define an organic radical. Name three.
5. Define constitution. Illustrate it by the empirical, rational, and graphic formulas of alcohol.

6. Name the nine important groups of organic compounds.

7. Review the general properties of hydrocarbons (see Chapter XV).

Name four hydrocarbons.

8. Define an alcohol. Discuss the constitution of alcohols.

9. Describe the preparation of methyl alcohol. State its properties and uses. Why is it called (*a*) methyl alcohol, and (*b*) wood alcohol?

10. State (*a*) the properties, and (*b*) the uses of ethyl alcohol.

11. What is (*a*) alcohol, (*b*) ethyl alcohol, (*c*) absolute alcohol, (*d*) methylated spirit, (*e*) proof spirit?

12. What is fermentation? What are ferment?

13. Describe the preparation of alcohol. Discuss the preparation, composition, and properties of (*a*) wines and beers, and (*b*) distilled liquors.

14. What are aldehydes? How are they related to alcohols and to hydrocarbons?

15. Describe the preparation and properties of (*a*) acetic aldehyde, and (*b*) formic aldehyde. State the uses of the latter. What is its commercial name?

16. What are ethers? How are they related to alcohols?

17. Describe the preparation, and state the properties and uses of ordinary ether.

18. What are organic acids? Illustrate (by acetic acid) their relation to hydrocarbons, alcohols, and aldehydes.

19. Describe the manufacture of acetic acid. State (*a*) its properties, and (*b*) its uses.

20. What is (*a*) pyroligneous acid, (*b*) glacial acetic acid, (*c*) wood vinegar, (*d*) commercial acetic acid?

21. Discuss the composition of acetic acid.

22. What is vinegar? Describe its manufacture. State its properties and uses.

23. What are acetates? State their general properties. Describe four, and state their uses.

24. Name three other acids (besides acetic) in the fatty acid series. Why is this series so called?

25. State the occurrence, properties, and uses of (*a*) oxalic acid, (*b*) lactic acid, (*c*) tartaric acid, (*d*) citric acid. Where is malic acid found?

26. What is (*a*) argol, (*b*) crude tartar, (*c*) cream of tartar, (*d*) tar-emetic?

## Some Common Organic Compounds. 435

27. Review baking powder (see Sodium Bicarbonate).
28. What are ethereal salts? How are they formed? Where are they found? Describe ethyl acetate. Name three other ethereal salts and state their properties.
29. What is the test for (a) alcohol, and (b) acetic acid?
30. State clearly the general relations of fats to glycerine and soap.
31. Name the chief ingredients of fats and oils. What is (a) tallow, (b) butter, (c) oleomargarine, (d) stearin?
32. Describe the preparation of glycerine. State its properties and uses.
33. Discuss the constitution of glycerine. State the properties and uses of (a) nitroglycerine, and (b) dynamite.
34. What is soap? Describe its general method of manufacture. What is the chemistry of its manufacture? What fats and alkalies are used in making soap? Describe (a) the cold process, and (b) the boiling process of soap making.
35. What are carbohydrates? Why is this term used? Name several carbohydrates.
36. What are sugars? Name several.
37. Discuss the distribution of cane sugar. State its properties. What is (a) cane sugar, (b) sucrose, (c) saccharose, (d) barley sugar, (e) caramel? For what is the last used?
38. Describe the preparation of raw sugar from (a) sugar cane, and (b) sugar beets.
39. Describe the refining of sugar.
40. What is (a) granulated sugar, (b) brown sugar, (c) molasses?
41. What is the sugar of milk? What is its scientific name? For what is it used?
42. What is the formula of glucose? What other names has glucose? Where is glucose found? What sugar is closely related to glucose? How is glucose formed from cane sugar? State the equation for the reaction.
43. How is commercial glucose prepared? What is (a) commercial grape sugar, and (b) "glucose"? State the properties and uses of commercial glucose.
44. Describe the test for sugar.
45. Discuss the distribution of starch. Describe starch. State its properties. What is the test for starch?
46. How is starch prepared? State its uses.

47. What is the simplest formula of starch? How does it differ from the formula of (a) cane sugar, and (b) glucose?
48. What is dextrin? How is it prepared? For what is it used?
49. Discuss the chemistry of bread making.
50. What is cellulose? Describe pure cellulose. State its properties.
51. What is (a) parchment paper, (b) gun cotton, (c) collodion?
52. What is the chief constituent of paper? Describe the manufacture of paper.
53. State the source of benzene. State its properties. What is (a) benzol, and (b) benzine?
54. To what class of organic compounds does benzene belong? Why is it such an important compound?
55. What is the chemical relation of benzene to (a) toluene, (b) nitrobenzene, (c) aniline, (d) phenol, (e) benzoic acid?
56. Describe nitrobenzene. What is its chief use?
57. Describe aniline. How is it prepared? For what is it used?
58. Describe phenol. What is its source and use? What is its common name?
59. State briefly the relation of phenol to (a) picric acid, (b) picrates, (c) hydroquinone, (d) pyrogallic acid. What is the use of each?
60. Describe briefly benzoic acid and benzoic aldehyde.
61. Describe salicylic acid. State the use of this acid.
62. Describe naphthalene. What is its popular name? State its uses.
63. Describe anthracene. State its use. What is alizarin?
64. What are glucosides? Discuss (a) the occurrence, (b) the properties, and (c) the uses of tannin. What is (a) ink, and (b) leather?
65. What are alkaloids? Name six. What is their chief property?

#### PROBLEMS.

1. Alcohol is 0.8 as heavy as water. What is the weight of 1200 cc. of alcohol?
2. If 10 gm. of pure alcohol are burned, what weight of each product is formed? (Equation is  $C_2H_6O + 3O_2 = 2 CO_2 + 3 H_2O$ .)
3. Calculate the percentage composition of (a) alcohol ( $C_2H_6O$ ), (b) acetic acid ( $C_2H_4O_2$ ), (c) cane sugar ( $C_{12}H_{22}O_{11}$ ).
4. Calculate the simplest formulas of the substances having the composition: (a) carbon = 40, hydrogen = 6.67, oxygen = 53.33; (b) carbon = 15.8, hydrogen = 5.26, nitrogen = 36.84, sulphur = 42.1; (c) carbon = 54.55, hydrogen = 9.09, oxygen = 36.36.

## APPENDIX.

**1. The Metric System.**—The fundamental unit of this system of weights and measures is the **meter**. It is the unit of length, and is 39.37 inches long.

The meter and the other units have multiples and submultiples, which are designated by prefixes attached to the particular unit. The multiple prefixes are *deca-*, *hecto-*, and *kilo-*, equivalent respectively to 10, 100, and 1000. The submultiple prefixes are *deci-*, *centi-*, and *milli-*, which correspond respectively to 0.1, 0.01, and 0.001.

The unit of weight is the **gram**. It is derived from the **kilogram**, which is the weight of a cubic decimeter of water at 4° C. A kilogram weighs about 2.2 pounds. Small weights are expressed in terms of the gram. Thus, the weight of an object weighing 2 grams, 2 centigrams, and 5 milligrams is 2.025 grams.

The unit of volume is the **liter**. It is equal to the capacity of the vessel containing a kilogram of water. A liter equals about one quart.

The relation between the units, multiples, and submultiples is shown in the —

TABLE OF THE METRIC SYSTEM.

LENGTH.	WEIGHT.	VOLUME.	NOTATION.
Kilometer	Kilogram	Kiloliter	1000.
Hectometer	Hectogram	Hectoliter	100.
Decameter	Decagram	Decaliter	10.
METER	GRAM	LITER	1.
Decimeter	Decigram	Deciliter	0.1
Centimeter	Centigram	Centiliter	0.01
Millimeter	Milligram	Milliliter	0.001

From this table it is evident that 10 milligrams equal 1 centigram, 10 centigrams equal 1 decigram, 10 decigrams equal 1 gram, and so on.

The relation of the metric system to weights and measures in common use is shown by the —

TABLE OF METRIC EQUIVALENTS.

1 meter	= 39.37 inches	1 inch	= 2.54 centimeters
1 kilometer	= 0.62 mile	1 mile	= 1.6 kilometers
1 centimeter = 0.39 inch		1 cubic inch	= 16.39 cubic centimeters
1 liter	= 0.908 quart (dry)	1 quart (liq.)	= 0.9465 liter
1 liter	= 1.056 quart (liq.)	1 pound (avoir.)	= 0.4536 kilogram
1 gram	= 15.432 grains	1 ounce (avoir.)	= 28.35 grams
1 kilogram	= 2.2 pounds (avoir.)	1 ounce (troy)	= 31.1 grams
1 metric ton	= 2204 pounds	1 grain (apoth.)	= 0.0648 gram

The passage from the English to the metric system may be accomplished by utilizing the —

TABLE OF METRIC TRANSFORMATION.

To Change	Multiply by
Inches to centimeters . . . . .	2.54
Centimeters to inches . . . . .	0.3937
Cubic inches to cubic centimeters . . . . .	16.387
Cubic centimeters to cubic inches . . . . .	0.061
Ounces to grams (avoir.) . . . . .	28.35
Grams to ounces (avoir.) . . . . .	0.0353
Grains to grams . . . . .	0.0648
Grams to grains . . . . .	15.43

The customary abbreviations of the common denominations are —

meter, m.	liter, l.	cubic centimeter, cc.
decimeter, dm.	kilogram, kg. or Kg.	milligram, mg.
centimeter, cm.	decigram, dg.	centigram, cg.

The preferable abbreviation for gram is gm. The same abbreviation is used for singular and plural, e.g. 1 m., 4 gm., 3 cm., 50 cc.

A convenient relation (true only in the case of water) to remember is 1 l. = 1 kg. = 1 cu. dm. = 1000 cc. = 1000 gm. = 2.2 lb.

## PROBLEMS.

1. What is the abbreviation of gram, centigram, liter, meter, cubic centimeter, centimeter, decimeter, milligram?
2. Express (a) 1 liter in cubic centimeters, (b) 2 l. in cc., (c) 1 meter in centimeters, (d) 250 cm. in dm., (e) 1 kg. in grams, (f) 250 gm. in mg.
3. Add 2 kg., 5 dg., 2 cg., 4 gm., and 7 mg., and express the sum in grams.
4. How many cc. in a liter?
5. What is the weight in grams of (a) 1 liter of water, (b) 250 cc., (c) 500 cc., (d) 721 cc.?
6. Express in grams (a) 721 kg., (b) 62 mg., (c) 245 cg., (d) 84 dg.
7. Express (a) 40 meters in inches, (b) 25 kilograms in pounds, (c) 54 grams in ounces, (d) 72 grams in grains, (e) 75 liters in quarts (liq.).

**2. The Thermometer** in scientific use is the **centigrade**. The boiling point of water on this thermometer is 100, and the freezing point is 0 (Fig. 8o). The equal spaces between these points are called degrees. The abbreviation for centigrade is C., and for degrees is °. Thus, the boiling point of water is 100° C. Degrees below zero are always designated as minus, e.g. -12° C., means 12 degrees below zero.

The thermometer in popular use is the **Fahrenheit**. On this instrument the boiling point of water is 212° and the freezing point is 32° above zero (Fig. 8o).

To change Fahrenheit degrees into the equivalent centigrade degrees, subtract 32 and multiply the remainder by  $\frac{5}{9}$ , or briefly—

$$C = \frac{5}{9}(F - 32).$$

To change centigrade degrees into the equivalent Fahrenheit temperature, multiply by  $\frac{9}{5}$  and add 32 to the product, or briefly—

$$F = \frac{9}{5}C + 32.$$

The point -273° C. is called **absolute zero**. Absolute temperature is reckoned from this point. Degrees on the absolute scale are found by adding 273 to the readings on the centigrade thermometer. Thus, 273° absolute is 0° C., 274° absolute is +1° C., etc.

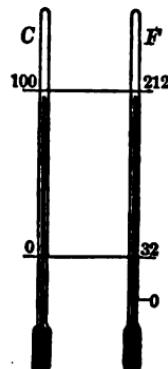


FIG. 8o.—Thermometers.

## PROBLEMS.

1. Change into Fahrenheit readings the following centigrade readings: (a) 60.5, (b) 40, (c) 92, (d) -5, (e) 0, (f) 100, (g) 860, (h) -40.
2. Change into centigrade readings the following Fahrenheit readings: (a) 207, (b) 180, (c) 0, (d) -30, (e) 212, (f) 100, (g) -40, (h) 270.
3. Express the following centigrade readings in absolute readings: (a) 0, (b) 24, (c) -13, (d) -260.

3. **Crystallization.**—Most substances in passing from a liquid or a gas into a solid assume a definite shape. This change is called **crystallization**, and the substances are said to **crystallize** or to form **crystals**. Crystals are produced by (1) evaporating a solution, (2) cooling a melted solid, or (3) cooling a vapor. Thus, salt crystals are formed by evaporating a salt solution; sulphur crystals, by melting and then cooling sulphur, and iodine crystals, by heating iodine in a test tube. These methods are called, respectively, evaporation, fusion, and sublimation.

As a rule each substance has an individual crystal form by which it can be distinguished. Although there are thousands of different crystals, all belong to one of six classes or systems. This classification is based upon two assumptions: (1) all crystals contain certain lines called axes, and (2) the surfaces or faces are grouped around the axes in definite positions. The axes connect angles, edges, or faces, which are similarly situated on opposite sides of the crystal. The bounding planes or faces are arranged symmetrically around the axes, which also determine (by their lengths and relative positions) the positions of the bounding planes. For example, the cube has three equal axes at right angles to one another, and terminating in the center of each of the six bounding surfaces.

The following is a brief description of the six systems of crystallization:—

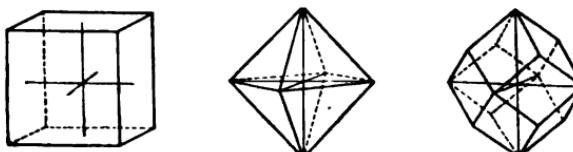


FIG. 81.—Isometric crystals (cube, octahedron, dodecahedron).

(1) **Isometric.**—This has three equal axes intersecting at right angles. The simplest forms are the cube, octahedron, and dodecahedron (Fig. 81). Substances crystallizing in this system are diamond, common salt, alum, fluor spar, iron pyrites, and garnet.

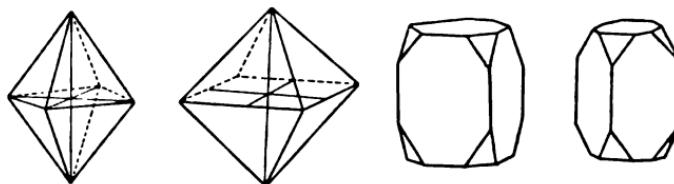


FIG. 82.—Tetragonal crystals.

(2) **Tetragonal.**—This has three axes at right angles; but one axis is shorter or longer than the other two, which are equal. The common forms are the prism, pyramid, and their combinations (Fig. 82). Tin dioxide and zircon form tetragonal crystals.



FIG. 83.—Orthorhombic crystals.

(3) **Orthorhombic.**—This has three unequal axes intersecting at right angles. Common forms are the prism, pyramid, and their combinations (Fig. 83). Potassium nitrate, barium sulphate, topaz, and native sulphur crystallize in this system (see Fig. 49).

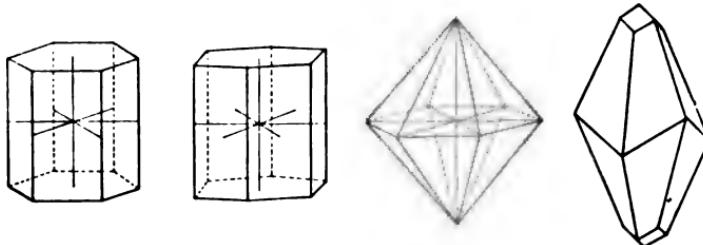


FIG. 84.—Hexagonal crystals.

(4) **Hexagonal.**—This has four axes: three are equal and intersect at  $60^\circ$  in the same plane; the fourth is longer or shorter than the others

and is at right angles to their plane. It is a complex system. Common forms are the prism, pyramid, rhombohedron, scalenohedron, and their combinations (Fig. 84). In this system are found quartz, calcite, beryl, corundum, and ice (see Figs. 5, 52, 61).

(5) **Monoclinic.** — This has three unequal axes: two cut each other obliquely, and the third is at right angles to the plane of the other two. Common forms are combinations of prisms. It is a complex system, but includes many substances, *e.g.* sulphur deposited by fusion, sodium carbonate, borax, gypsum, and ferrous sulphate (Fig. 85).



FIG. 85.—Monoclinic crystal.

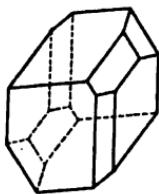


FIG. 86.—Triclinic crystals.

(6) **Triclinic.** — This has three unequal axes, all intersecting at oblique angles. Common forms are complex combinations. Copper sulphate, potassium dichromate, boric acid, and several minerals form triclinic crystals (Fig. 86).

**4. History and Biography.** — The biographical data and table given here will serve as a basis for this interesting branch of chemistry. Additional facts can be obtained from the historical books mentioned below (under "Reference Books").

**Arrhenius, Svante, 1859** —. Swedish physicist. Contributor to modern theory of solution.

**Avogadro, Amadeo, 1776–1856.** Italian chemist and physicist. Proposed in 1811 his hypothesis — equal number of molecules in equal volumes of all gases at same temperature and pressure.

**Balard, Antoine Jerome, 1802–1876.** French chemist. Discovered bromine in 1826.

**Becher, Johann Joachim, 1635–1682.** German physician. Discovered few facts, but collected and explained writings of others. Believed in alchemy, but made no search for gold. Laid foundations of phlogiston theory.

**Bergman, Torbern, 1735-1784.** Swedish chemist. Improved methods of chemical analysis. Believed in phlogiston. Studied minerals and organic acids. Contributed much to the industrial development of Sweden. Intimate friend of Scheele.

**Berthollet, Claude Louis, 1748-1822.** French chemist. Studied composition of ammonia, properties and nature of chlorine, hydrogen sulphide, and hydrocyanic acid. Explained chemical changes by "affinity." His discussion with Proust led to law of definite proportions.

**Berzelius, Johann Jacob, 1779-1848.** Swedish chemist. Determined many atomic weights. Introduced use of symbols. Discovered selenium, prepared silicon and several rare elements. Investigated law of multiple proportions, proposed dualistic theory and an electrochemical theory, improved experimental methods. Industrious investigator, prolific writer.

**Bessemer, Sir Henry, 1813-1898.** English metallurgist. Devised, in 1856, Bessemer process of making steel.

**Black, Joseph, 1728-1799.** Scotch chemist and physicist. Discovered carbon dioxide. Showed relation of this gas to carbonates of alkalies and alkaline earths. Opposed phlogiston theory. Teacher and friend of James Watt and Rutherford.

**Boyle, Robert, 1626-1691.** English philosopher. Announced law of effect of pressure on gases. Studied air and water. Opposed to alchemy. Views anticipated present conception of constitution of matter. Laid foundation of qualitative analysis.

**Bunsen von, R. W. E., 1811-1899.** German chemist. Studied blast furnace and developed gas analysis. Invented the burner, photometer, and battery bearing his name. With Kirchhoff (about 1860) devised the spectroscope, and by it developed spectrum analysis and discovered rubidium and caesium; improved the calorimeter; studied chemical action of light.

**Cannizzaro, Stanislao, 1826 —.** Italian chemist. Revived Avogadro's hypothesis in 1858, and thereby led to revision of atomic weights.

**Cavendish, Henry, 1731-1810.** English chemist. Discovered hydrogen, determined specific gravity of gases, showed (1) solubility of calcium carbonate in water containing carbon dioxide, (2) formation of water by burning of hydrogen. Determined composition of the atmosphere and of nitric oxide. Accepted phlogiston theory. He was parsimonious, eccentric, shy; trained mathematician and electrician; "the richest of the wise, and the wisest of the rich."

**Charles, Jacques Alex César, 1746-1822.** French physicist. Proposed law bearing his name.

**Courtois, Bernard, 1777-1838.** French chemist. Discovered iodine in 1811.

**Dalton, John, 1766-1844.** English chemist, physicist, and mathematician. Devised atomic theory. Discovered law of multiple proportions. "Dalton was often inaccurate as to facts, deficient in the details of chemical manipulations, and did not hold high rank as an experimenter; but he was good at drawing conclusions and at stating generalizations, his aim being the establishment of general, underlying laws." (Venable.)

**Davy, Sir Humphry, 1778-1829.** English chemist. Studied gases, demonstrated properties of nitrous oxide, determined composition of hydrochloric acid, studied iodine and chlorine, named latter. Isolated potassium, sodium, barium, calcium, and strontium by electrolysis, and studied action of electricity on water and on many other substances. Devised miner's safety lamp. "He was one of the most brilliant chemists the world has ever seen and the greatest England has produced."

**Dewar, James, 1842 —.** English chemist. Pioneer in the liquefaction of gases by modern methods. (See Hydrogen.)

**Dulong, Pierre Louis, 1785-1838.** French chemist and physicist. With Petit announced law of specific heats in 1819.

**Dumas, Jean Baptiste André, 1800-1884.** French chemist. Determined many atomic weights, gravimetric composition of water, composition of air. Investigated many organic compounds. Devised a method of determining vapor density. Excellent teacher, careful editor, and faithful public servant.

**Faraday, Michael, 1791-1867.** English chemist and physicist. Liquefied chlorine and other gases. Showed quantitative relation between electric current and chemical changes, and developed electrochemistry. Was Davy's assistant and successor in the Royal Institution. Popular lecturer, keen investigator, and ardent lover of science.

**Gay-Lussac, Joseph Louis, 1778-1850.** French chemist and physicist. Announced law of gas volumes in 1808. Worked on cyanogen, iodine, halogen acids, alkaline oxides, isolation of boron. Improved methods of analyzing organic compounds. Was pupil of Berthollet. "Was a trained chemist, capable of most accurate analytical work, and possessing scientific acumen in a very high degree." (Venable.)

**Glauber, Johann Rudolph, 1604-1668.** German chemist. Believed in alchemy. Discovered sodium sulphate, which even now bears his name. Suggested improvements in industrial chemistry.

**Graham, Thomas, 1805-1869.** British chemist. Studied diffusion of gases, acids of phosphorus, water of crystallization, and dialysis. Developed idea of basicity of acids.

**Hofmann von, August Wilhelm, 1818-1892.** German chemist. Studied organic chemistry exhaustively. Coal-tar industry arose largely from his work. Devised unique lecture apparatus, e.g. that for the electrolysis of water. Brilliant teacher, prolific investigator.

**Kirchhoff, Gustav Robert, 1824-1887.** German physicist. With Bunsen, devised spectroscope and founded principles of spectrum analysis.

**Lavoisier, Antoine Laurent, 1743-1794.** French chemist. Overthrew phlogiston theory, explained combustion, contributed many facts to a large number of chemical topics. Devised foundation of chemical nomenclature. Interpreted experiments of other chemists. Efficient public servant. Regarded by many as the founder of modern chemistry. Accused of appropriating public money and of "putting water in the people's tobacco," he was condemned by the infamous Robespierre, and publicly guillotined.

**Liebig von, Justus, 1803-1873.** German chemist. Laid foundations of agricultural and organic chemistry. Eminent teacher.

**Mendeleeff, Dmitri Ivanovitch, 1834-1907.** Russian chemist. Announced periodic law in 1868.

**Meyer, Lothar 1830-1895.** German chemist. Contributed to establishment of periodic law.

**Moliéan, Henri, 1852-1907.** French chemist. Isolated fluorine, devised and perfected electric furnace, prepared artificial diamonds, rare metals, and refractory compounds.

**Ostwald, Wilhelm, 1853 —.** German chemist. Contributor to modern theory of solution. Eminent teacher and prolific writer.

**Petit, Alexis Thérèse, 1791-1820.** French physicist. (See Dulong.)

**Priestley, Joseph, 1733-1804.** English chemist and theologian. Student of electricity, light, and gases. Discovered oxygen. Devised pneumatic trough. His political and religious views were so freely expressed that he was obliged to leave England. Came to America in 1795. Died at Northumberland near Philadelphia, Pennsylvania.

**Proust, Louis Joseph, 1755-1826.** French chemist. Defended law of definite proportions in a long controversy with Berthollet

"One of the good results of this controversy was to bring about a definition of compounds and mixtures, and a clear distinction between them. In course of it, also, Proust discovered the hydroxides, a class of compounds until then confused with the oxides." (Venable.)

**Prout, William, 1785-1850.** English physician. Advanced in 1815 the hypothesis that the atomic weights of all elements are whole numbers.

**Ramsay, William, 1852 —.** English chemist. Discovered argon, helium, neon, krypton, and xenon.

**Rutherford, Daniel, 1749-1819.** Scotch botanist and physician. Discovered nitrogen in 1772. Pupil of Black.

**Scheele, Carl Wilhelm, 1742-1786.** Swedish chemist. Discovered chlorine, ammonia, manganese, baryta, many acids (organic and inorganic), and oxygen (independently of Priestley). Isolated and studied borax, glycerine, Prussian blue, microcosmic salt. Improved the methods of preparing many substances. Was very poor. Friend and companion of Bergman. Achieved marvelous results with simple appliances. Believed in phlogiston.

**Stahl, George Ernst, 1660-1734.** German physician and chemist. Revived and extended Becher's ideas of combustion. Introduced the name *phlogiston*. Strongly advocated this theory. Successful teacher and writer.

**Stas, Jean Servais, 1813-1891.** Belgian chemist. Determined accurately many atomic weights. Pupil of Dumas. Overthrew Prout's hypothesis.

**Van Helmont, Jean, 1577-1644.** Dutch chemist. Studied gases, and discovered carbon dioxide. Had imperfect but introductory views on physiological chemistry, indestructibility of matter, and elements. Believed in the *alkahest* or universal solvent.

**Van't Hoff, Jacobus Hendricus, 1852 —.** Dutch chemist. Contributor to chemistry of space relations of atoms and to modern theory of solution.

**Wöhler, Friedrich, 1800-1882.** German chemist. Isolated aluminium and beryllium. Worked on boron, silicon, and many organic substances. Discovered isomerism. Overthrew barrier between organic and inorganic chemistry. Was fellow-worker with Liebig, pupil of Berzelius, and influential teacher of many famous chemists.

## CHRONOLOGICAL TABLE OF FAMOUS CHEMISTS.

Greeks	Galen	Aristotle		
Middle Ages	Geber	Avicenna	Albertus Magnus	Roger Bacon
	8th Century	978-1036	1193-1280	1214-1294
	Raymond Lulli		Basil Valentine	
	1235-1315		1394	—
14th to 16th Centuries.	Paracelsus 1493-1541	Agricola 1494-1555	Libavius 1540-1616	Van Helmont 1577-1644
17th and 18th Centuries.	Glauber 1604-1668	Boyle 1626-1691	Becher 1635-1682	Hooke 1635-1702
	Mayow 1645-1679	Stahl 1660-1734	Boerhaave 1668-1738	Hales 1677-1761
18th and 19th Centuries.	ENGLISH. Black 1728-1799	Cavendish 1731-1810	Priestley 1733-1804	
	Dalton 1766-1844	Davy 1778-1829	Faraday 1791-1867	
	FRENCH. Lavoisier 1743-1794	Berthollet 1748-1822	Proust 1755-1826	
	Gay-Lussac 1778-1850			
	SWEDISH. Bergman 1735-1784	Scheele 1742-1786	Berzelius 1779-1848	
19th Century.	ENGLISH. Graham 1805-1869	FRENCH. Dumas 1800-1884	BELGIAN. Stas 1813-1891	
	GERMAN. Wöhler 1800-1882	Liebig 1803-1873	Bunsen 1811-1899	
	Hofmann 1818-1892			

5. **Atomic Weights.**—The following table of atomic weights is based upon the latest available Table of International Atomic Weights.

TABLE OF ATOMIC WEIGHTS.

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	
		International.	Approximate.
Aluminium . . . . .	Al	27.1	27
Antimony . . . . .	Sb	120.2	120
Argon . . . . .	A	39.9	—
Arsenic . . . . .	As	75.0	75
Barium . . . . .	Ba	137.37	137
Bismuth . . . . .	Bi	208.0	208
Boron . . . . .	B	11.0	11
Bromine . . . . .	Br	79.92	80
Cadmium . . . . .	Cd	112.40	112
Cæsium . . . . .	Cs	132.81	—
Calcium . . . . .	Ca	40.09	40
Carbon . . . . .	C	12.00	12
Cerium . . . . .	Ce	140.25	—
Chlorine . . . . .	Cl	35.46	35.5
Chromium . . . . .	Cr	52.1	52
Cobalt . . . . .	Co	58.97	59
Columbium . . . . .	Cb	93.5	—
Copper . . . . .	Cu	63.57	63.5
Dysprosium . . . . .	Dy	162.5	—
Erbium . . . . .	Er	167.4	—
Europium . . . . .	Eu	152.0	—
Fluorine . . . . .	F	19.0	19
Gadolinium . . . . .	Gd	157.3	—
Gallium . . . . .	Ga	69.9	—
Germanium . . . . .	Ge	72.5	—
Glucinum . . . . .	Gl	9.1	—
Gold . . . . .	Au	197.2	197
Helium . . . . .	He	4.0	—
Hydrogen . . . . .	H	1.008	1
Indium . . . . .	In	114.8	—
Iodine . . . . .	I	126.92	127
Iridium . . . . .	Ir	193.1	—
Iron . . . . .	Fe	55.85	56
Krypton . . . . .	Kr	81.8	—
Lanthanum . . . . .	La	139.0	—
Lead . . . . .	Pb	207.10	207
Lithium . . . . .	Li	7.00	7
Lutecium . . . . .	Lu	174.0	—
Magnesium . . . . .	Mg	24.32	24
Manganese . . . . .	Mn	54.93	55
Mercury . . . . .	Hg	200.0	200

TABLE OF ATOMIC WEIGHTS (*Continued*).

ELEMENT.	SYMBOL.	ATOMIC WEIGHT.	
		International.	Approximate
Molybdenum . . . . .	Mo	96.0	—
Neodymium . . . . .	Nd	144.3	—
Neon . . . . .	Ne	20.0	—
Nickel . . . . .	Ni	58.68	59
Nitrogen . . . . .	N	14.01	14
Osmium . . . . .	Os	190.9	—
Oxygen . . . . .	O	16.00	16
Palladium . . . . .	Pd	106.7	—
Phosphorus . . . . .	P	31.0	31
Platinum . . . . .	Pt	195.0	195
Potassium . . . . .	K	39.10	39
Praseodymium . . . . .	Pr	140.6	—
Radium . . . . .	Ra	226.4	—
Rhodium . . . . .	Rh	102.9	—
Rubidium . . . . .	Rb	85.45	—
Ruthenium . . . . .	Ru	101.7	—
Samarium . . . . .	Sa	150.4	—
Scandium . . . . .	Sc	44.1	—
Selenium . . . . .	Se	79.2	—
Silicon . . . . .	Si	28.3	28
Silver . . . . .	Ag	107.88	108
Sodium . . . . .	Na	23.00	23
Strontium . . . . .	Sr	87.62	87
Sulphur . . . . .	S	32.07	32
Tantalum . . . . .	Ta	181.0	—
Tellurium . . . . .	Te	127.5	—
Terbium . . . . .	Tb	159.2	—
Thallium . . . . .	Tl	204.0	—
Thorium . . . . .	Th	232.42	—
Thulium . . . . .	Tm	168.5	—
Tin . . . . .	Sn	119.0	119
Titanium . . . . .	Ti	48.1	—
Tungsten . . . . .	W	184.0	—
Uranium . . . . .	U	238.5	—
Vanadium . . . . .	V	51.2	—
Xenon . . . . .	Xe	128.0	—
Ytterbium (Neoytterbium) . . . . .	Yb	172.0	—
Yttrium . . . . .	Y	89.0	—
Zinc . . . . .	Zn	65.37	65
Zirconium . . . . .	Zr	90.6	—

**6. Reference Books and Supplementary Reading.**—The list of books given below will serve as the basis of a chemical library. The starred (\*) titles indicate books intended for the teacher, though many parts of these books are not beyond the grasp of pupils. The library should contain at least numbers 1, 5, 8, 10, 18, 20, 22, 24. Additional titles can be found in (1) List of Books in Chemistry, L. E. Knott Apparatus Co., Boston, Mass.; (2) Smith and Hall's Teaching of Chemistry and Physics, p. 218; (3) NEWELL'S EXPERIMENTAL CHEMISTRY, APP. C, II.

1. Text-Book of Inorganic Chemistry, Newth. Longmans, Green, & Co., 682 pp., \$1.75.
- \*2. General Inorganic Chemistry, Freer. Allyn & Bacon, Boston, 559 pp., \$3.
- \*3. Text-Book of Inorganic Chemistry, Holleman. John Wiley & Sons, 458 pp., \$2.50.
4. Physical Chemistry for Beginners, Van Deventer. John Wiley & Sons, 154 pp., \$1.50.
5. Chemical Theory for Beginners, Dobbin and Walker. The Macmillan Co., 236 pp., \$.70.
- \*6. Introduction to Physical Chemistry, Walker. The Macmillan Co., 332 pp., \$3.
7. The Birth of Chemistry, Rodwell. The Macmillan Co., 135 pp., \$1.
8. Short History of Chemistry, Venable. D. C. Heath & Co., 172 pp., \$1.
9. Faraday as a Discoverer, Tyndall. D. Appleton & Co., 171 pp., \$1.
10. Short History of Natural Science, Buckley. D. Appleton & Co., 467 pp., \$2.
11. Heroes of Science—Chemists, Muir. Thomas Nelson & Son, 350 pp., \$1.50.
- \*12. Essays in Historical Chemistry, Thorpe. The Macmillan Co., 582 pp., \$4.
13. Humphry Davy, Thorpe. The Macmillan Co., 240 pp., \$1.25.
14. John Dalton, Roscoe. The Macmillan Co., 216 pp., \$1.25.
15. Michael Faraday, Thompson. The Macmillan Co., 308 pp., \$1.25.
- \*16. Alembic Club Reprints, University of Chicago Press, \$.40 each.  
(1) Experiments on Magnesia Alba. (2) Foundations of the Atomic

Theory. (3) Experiments on Air. (4) Foundations of the Molecular Theory. (6) Decomposition of the Fixed Alkalies. (7) (8) Discovery of Oxygen. (9) Elementary Nature of Chlorine. (13) Early History of Chlorine.

\*17. Organic Chemistry, Remsen. D. C. Heath & Co., 426 pp., \$1.30.

18. Outlines of Industrial Chemistry, F. H. Thorp. The Macmillan Co., 528 pp., \$3.50.

\*19. Practical Electro-Chemistry, Blount. The Macmillan Co., 374 pp., \$3.25.

20. Chemistry in Daily Life, Lassar-Cohn. J. B. Lippincott Co., 336 pp., \$1.75.

21. The Soil, King. The Macmillan Co., 400 pp.

22. Story of a Piece of Coal, Martin. D. Appleton & Co., 165 pp., \$ .40.

23. Chemical History of a Candle, Faraday. Harper & Bros., 223 pp., \$1.00.

24. Minerals and How to Study Them, E. S. Dana. John Wiley & Sons, 380 pp., \$1.25.

\*25. Teaching of Chemistry and Physics, Smith and Hall. Longmans, Green & Co., 384 pp., \$1.50.

26. Story of Nineteenth-Century Science, Williams. Harper & Bros., 475 pp., \$2.50.

27. Stories of Industry, Vol. I, Chase and Clow. Educational Publishing Co., Boston, 172 pp., \$.40.

Scientific American, Munn & Co., New York. \$3.00 yearly; single copies, 8 cents.

School Science, Ravenswood, Chicago, Illinois. \$2.00 yearly (9 issues); single copies, 25 cents.

Popular Science Monthly, The Science Press, New York. \$3.00 yearly; single copies, 30 cents.



# DESCRIPTIVE CHEMISTRY

BY

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## PART II EXPERIMENTS

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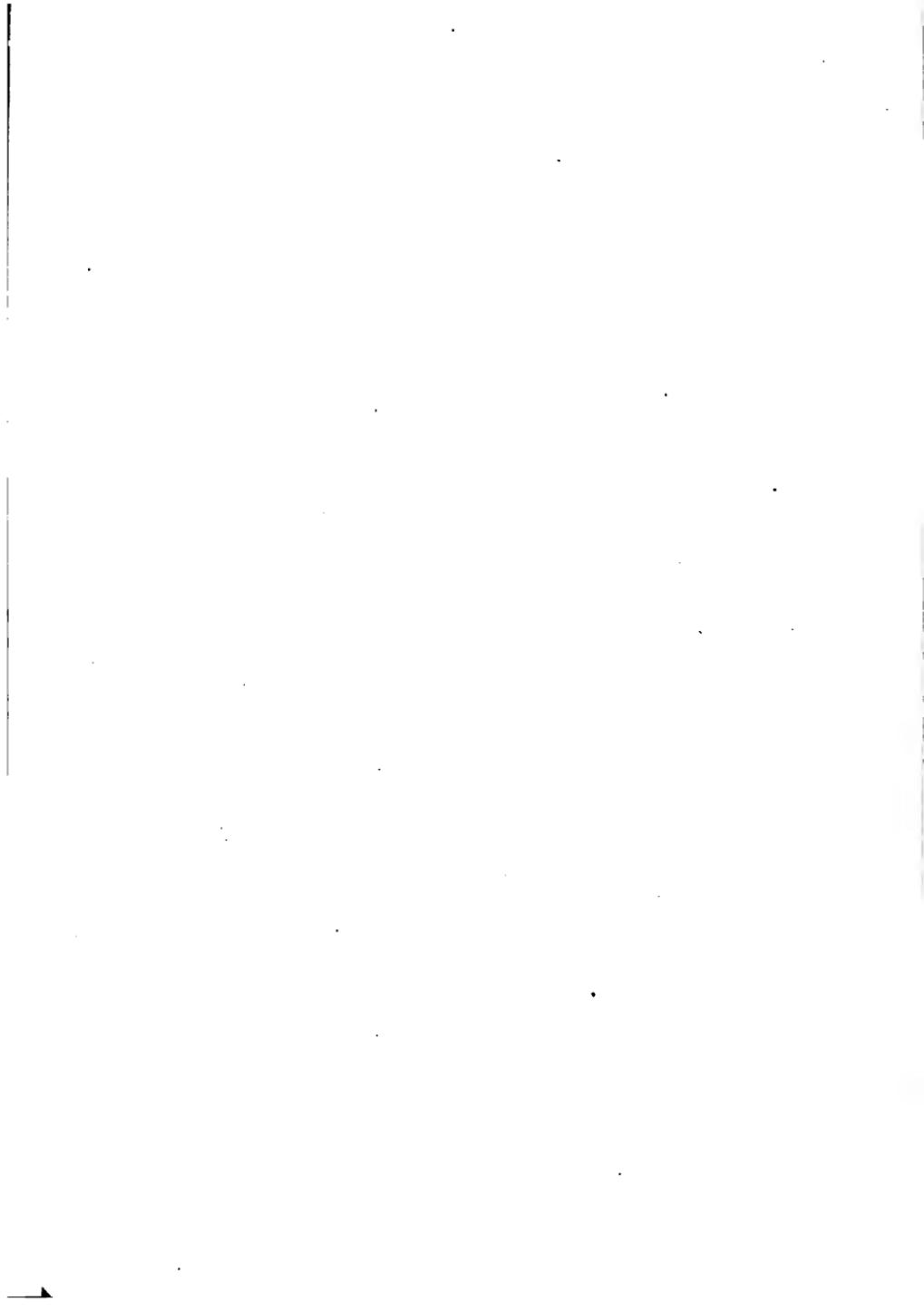
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**PART II**

**EXPERIMENTS**



## INTRODUCTION.

**1. The Bunsen burner** is used as the source of heat in most chemical laboratories (Fig. 87). It is attached to the gas cock by a piece of rubber tubing. When the gas is turned on, the current of gas draws air through the holes at the bottom of the tube, and this mixture when lighted burns with an almost colorless, *i. e.* non-luminous, flame. It is a hot flame and deposits no soot. The burner is lighted by turning on the gas full and holding a lighted match in the gas about 5 centimeters (2 inches) above the top of the burner. If the flame is not colorless, or nearly so, turn the ring at the bottom of the burner until the flame is a faint blue. The colorless flame should be used in all experiments unless the directions state otherwise, and should be from 5 to 10 centimeters (2 to 4 inches) high. The hottest part of the flame is near the top.

**2. Heating.** — The following directions should be observed in heating with the Bunsen burner:—

(1) The burner should always be lighted before any piece of apparatus is held over it, or before it is placed beneath a wire gauze which supports a dish or flask.

(2) Glass and porcelain apparatus should not be heated when empty nor over a bare or free flame even if they contain something — unless directions so state. Vessels requiring a support should be placed on a wire gauze which stands on the ring of an iron stand, and heated gradually from beneath. Hot vessels should be heated and cooled gradually; if removed from the gauze while hot, they should be placed on a block of wood or piece of asbestos board — never on a cold surface.

(3) Many experiments require the heating of test tubes. These tubes should be dry on the outside before being heated. The temperature of a test tube containing a solid should be raised gradually by moving it in and out of the flame, or by holding it in the flame and roll-



FIG. 87. — Bunsen burner.

ing it slightly between the thumb and forefinger. Special care must be taken to distribute the heat evenly. If the test tube contains a liquid, as is usually the case, only that part containing the liquid should be heated; the test tube should also be inclined so that the greatest heat is not directed upon the thin bottom.

When the liquid begins to boil, the test tube should be removed from the flame for an instant or held over it. In some experiments test tubes can be held between the thumb and forefinger without discomfort. If they are too hot to handle, a test-tube holder may be used (Fig. 88).

**3. Cutting and bending Glass Tubing.**—(a) *Cutting.* Determine the length needed, lay the tube on the desk, and with a forward stroke of a triangular file make a short but deep scratch where the tube is to be cut. Grasp the tube in both hands, and hold the thumbs together behind the scratch. Now push gently with the thumbs, pull at the same time with the hands, and the tube will break at the desired point. The sharp ends should be smoothed by rubbing them with emery paper or by rotating them slowly in the Bunsen flame until a yellow color is distinctly seen or until the ends become red-hot.



FIG. 89.—Wing-top attachment for the flattened Bunsen burner. The flattened Bunsen flame should be slightly yellow and about 7 centimeters (2.5 inches) wide for ordinary bends. A right-angle bend is made as follows: Determine the point at which the tube is to be bent. Grasp the tube in both hands, and hold it so that the part to be bent is directly over the

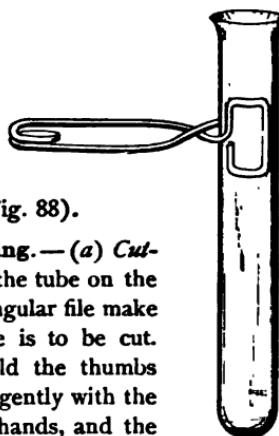


FIG. 88.—  
Test tube and  
holder.

(b) *Bending.* Glass tubes are bent in a flat flame. An ordinary illuminating gas flame may be used, but the Bunsen flame can be flattened by a wing-top attachment (Fig. 89), which slips over the top of the burner tube.



FIG. 90.—Bending a tube into a right angle—I.

flame. Slowly rotate it between the thumbs and forefingers, and gradually lower it into the position shown in Figure 90. Continue to rotate it until the glass feels soft and ready to yield. Then remove it from the flame, and slowly bend it into a right angle, as shown in Figure 91. It is convenient to have at hand a block of wood or some other right-angled object to assist the eye in completing the bend into an exact right angle. If a Bunsen flame is used, the bent part of the tube should be annealed, *i.e.* cooled slowly. This is done by holding it in a yellow flame until it becomes coated with soot. It should then be placed on a block of wood, and when cold wiped clean. Tubes can be bent into an oblique angle by heating them through about twice the space required for a right angle; a very slight bend, however, is often made by holding the tube *across* the flame and heating a short space. Glass tubes which have been correctly bent never have flattened curves; nor are they twisted, *i.e.* all parts lie in the same plane.

(c) *Drawing.* Glass tubes can be drawn to a finer bore or into two pointed tubes as follows: Heat the glass as in (b) through about 2.5 centimeters (1 inch) of its length, remove from the flame and slowly pull it apart a short distance; let it cool for a few seconds, and then pull it quickly to the desired length.

The operation is well illustrated by making a glass stirring rod. Select a piece of rod about 25 centimeters (10 inches) long and .5



FIG. 91.—Bending a tube into a right angle—II.

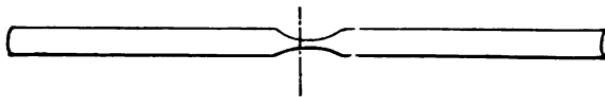


FIG. 92.—Stirring rods ready to be cut.

centimeter ( $\frac{5}{16}$  inch) in diameter. Heat it in the middle in the ordinary—not flat—Bunsen flame, and when soft draw it out slowly into the shape shown in Figure 92. Cut it into two rods by making a slight scratch where the dotted line indicates. Round off the rough edges by heating them slightly in the flame.

**4. Filtering.** — A solid may be separated from a liquid by filtering. A circular piece of porous paper is folded to fit a glass funnel, and when the mixture is poured upon this paper, the solid—the residue or precipitate—is retained, while the liquid—the filtrate—passes through and may be caught in a test tube or any other vessel. The filter paper is prepared for the funnel by folding it successively into the shapes shown in Figures 93 and 94, and then opening the folded paper so that three thicknesses are on one side and one on the other (Fig. 95). The cone-shaped paper is next placed in the funnel and wet with water,



FIG. 93.—Folded filter paper—I.

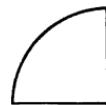


FIG. 94.—Folded filter paper—II.



FIG. 95.—Folded filter paper ready for funnel.

so that it will stick to the sides of the funnel and filter rapidly. The paper should never extend above the edges of the funnel, but its apex should always project slightly into the stem. The liquid to be filtered should be poured down a glass rod which touches the edge of the test tube; the lower end of the rod should just touch the paper inside the funnel, so that the liquid will run down the side and thereby avoid bursting the apex of the filter paper. It is also advisable to adjust the apparatus so that the end of the stem of the funnel rests against the side of the vessel catching the filtrate. A funnel can be supported by standing it in a test tube, a bottle, or the ring of an iron stand.

**5. Constructing and arranging Apparatus.** — The various parts of an apparatus should be collected, prepared, and put together before starting the experiment in which the apparatus as a whole is used. The different parts which are to fit each other should be selected and arranged so that all joints are gas-tight, and as a final precaution the apparatus should be tested for leaks. All leaks should be stopped up before the apparatus is used. The following hints will be helpful: —

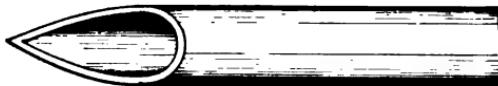


FIG. 96.—Rubber tube cut at an angle.

(1) *To insert a glass tube into rubber tubing.* Cut the rubber tubing at an angle, as shown in Figure 96, moisten the smoothed end of the glass

tube with water, place the end of the glass tube in the angular-shaped cavity so that both tubes are at about a right angle, and then slip the rubber tube slowly up and over the end of the glass tube. If the glass tube is large or the rubber stiff, the rubber tube must be held firmly between the thumb and forefinger to keep it from slipping off until it is securely adjusted.

(2) *To fit a glass tube to a stopper.* Moisten the end with water and grasp the tube firmly about 3 centimeters (1 inch) from the end; hold the stopper between the thumb and forefinger of the other hand, and work the tube into the hole by a gradual rotary motion. Proceed in the same manner if the tube is to be pushed through the stopper. *Never* point the tube toward the palm of the hand which holds the stopper. *Never* grasp a safety tube or any bent tube at the bend when inserting it into a stopper—it may break and cut the hand severely.

(3) *To bore a hole in a cork.* Rubber stoppers are preferable, but if corks are used, they can be bored as follows: Select a cork free from cracks or channels and use a borer which is one size smaller than the desired hole. Hold the cork between the thumb and forefinger, press the larger end against a firm but soft board, and slowly push the borer by a rotary movement through the cork, taking care to keep the borer perpendicular to the cork. If the hole is too small, enlarge it with a round file. If corks are used instead of rubber stoppers, the apparatus should always be tested before use by blowing into it, stopping of course all legitimate outlets. A poor cork often means a failure, to say nothing of wasted time.

(4) *To make a platinum test wire.* Rotate one end of a piece of glass rod, about 10 centimeters (4 inches) long, in the flame until it softens. At the same time grasp a piece of platinum wire about 7 centimeters (3 inches) long firmly in the forceps about 1 centimeter (.5 inch) from the end, and hold it in the flame. When the rod is soft enough, gently push the hot wire into the rod. Cool the rod gradually

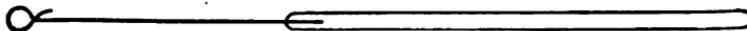


FIG. 97.—Platinum test wire.

by rotating it in the flame. The completed wire is shown in Figure 97. If a glass tube is used instead of a rod, it should be drawn out to a very small diameter (see § 3 (c)) before inserting the platinum wire, but in other respects the two operations are practically identical.

**6. Manipulation.**—Ability to use apparatus rapidly, accurately, and neatly is acquired only by experience, but the following suggestions will facilitate the acquisition of this needful skill:—

(1) *Pouring liquids and transferring solids.* (a) Liquids can be

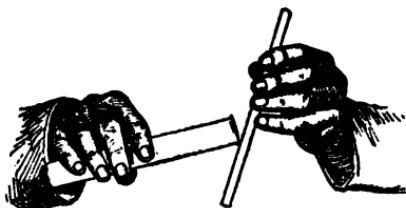


FIG. 98.—Pouring a liquid down a glass rod.

containing a solid without disturbing the solid. (b) Liquids can often be poured from a bottle by holding the bottle as shown in Figure 99. Notice that the stopper and bottle are held in the same hand. This is accomplished by holding the palm of the hand upward and removing the stopper by grasping it between the fingers before the bottle is lifted. All stoppers should be removed this way when possible, and not laid down, because the impurities adhering to the stopper may run down into the bottle and contaminate the solution. The drop on the lip of the bottle should be touched with the stopper before the latter is put into the bottle; this simple operation prevents the drop from running down the outside of the bottle upon the label or upon the shelf. (c) Solids should never be poured directly from a large bottle into a test tube, retort, or similar vessel. A convenient method is as follows: Rotate the bottle slowly so that the

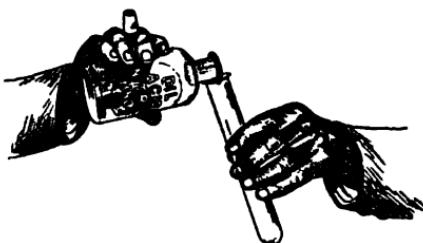


FIG. 99.—The way in which a glass stopper should be held while a liquid is being poured from a bottle.

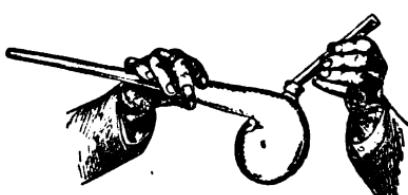


FIG. 100.—Pouring a solid into a vessel with a small opening.

solid will roll out in small quantities; catch the solid on a narrow strip of paper folded lengthwise, and slide the solid from the paper into the desired vessel. The last part of the operation is shown in Figure 100.

(2) *Collecting gases.* Gases are usually collected over water by means of a pneumatic trough, a common form of which is shown in Figure 102. The vessel to be filled with gas is first filled with water, covered with a piece of filter paper, inverted, and placed mouth downward on the shelf of the trough, which is previously filled with water just above the shelf. The paper is then removed, and the vessel slipped over the hole in the shelf of the trough. Glass plates instead of filter paper may be used to cover the bottle. The gas which is evolved in the generator passes through the delivery tube, and bubbles up through the water into the bottle, forcing the water out of the bottle as it rises. All gases insoluble in water are thus collected. Some heavy gases, such as hydrochloric acid, chlorine, and sulphur dioxide, are collected by allowing the gas to flow downward into an empty bottle, and displace the air in the bottle, *i.e.* by *downward displacement*. Ammonia and other light gases are usually collected by allowing the gas to flow upward into a bottle, *i.e.* by *upward displacement*.

(3) *Weighing and measuring.* These operations are best learned by personal direction from the teacher, together with patient application of a few general principles. The following hints, however, will be of assistance:—

(a) Learn as soon as possible how to use the scales and interpret the weights.

(b) Always leave the scales and weights in a clean, usable condition.

(c) Substances should not be weighed on the bare scale pan, but on a smooth piece of paper creased on the edges or along the middle. Take the solid from the bottle with a *clean* spoon or spatula or pour by rotating the bottle as described in § 6 (c). In many experiments only approximate quantities are needed. If you weigh out too much, do not put it back into the bottle, but throw it away or put it into a special bottle.

(d) Liquids are measured in graduated cylinders. The lowest point of the curved

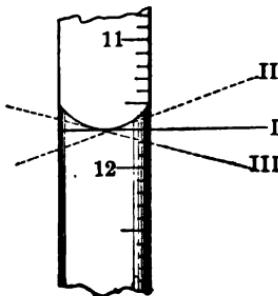


FIG. 101.—Meniscus. Correct reading is along line I.

surface of the liquid is its correct height (see Fig. 101). The average ordinary test tube holds about 30 cubic centimeters, while the large test tube—so often mentioned in the succeeding experiments—holds about 75 cubic centimeters. Time can be saved by remembering these volumes.

(e) All measurements in this book are in the metric system (see App. § 1). The common denominations, their abbreviations, and English equivalents should be learned.

**7. Smelling and Tasting.**—Unfamiliar substances should never be tasted or smelled except according to directions, and even then with the utmost caution. Never inhale a gas vigorously, but waft it gently with the hand toward the nose. Taste acids, etc., by touching a minute portion to the tip of the tongue, and as soon as the sensation is detected, reject the solution at once—never swallow it.

## EXPERIMENTS.

### PHYSICAL AND CHEMICAL CHANGES.

#### **Experiment 1.—Physical Change.** *Materials:* Salt, glass rod.

Dissolve a little salt in a test tube one fourth full of water. Dip a glass rod into the liquid and taste it. Has the characteristic property of the salt been changed? Dip the rod into the liquid again, and hold it *over* the flame of the Bunsen burner. As the water evaporates, a white solid appears. Taste it. What is it? Have its original properties been destroyed? What kind of a change did they undergo? What kind of a change did the salt undergo? What caused the change?

#### **Experiment 2.—Physical Change.** *Material:* Iodine.

Drop a small crystal of iodine into a dry test tube, and gently heat the bottom. As the violet vapor arises, remove the tube from the flame and let it cool. Do the crystals which form near the top resemble the original crystal? When gently heated, do they change into the violet vapor? How has the iodine crystal been changed? What caused the change? Do the original properties reappear after the cause has been removed? What kind of a change has the iodine undergone?

#### **Experiment 3.—Physical Change.** *Material:* Glass rod.

Rub a glass rod briskly on a piece of cloth, and hold it near small bits of dry paper. Describe what happens. After a moment touch the paper again. Is the result the same? Try again. Are the original properties of the glass restored when the cause of its change is removed? What kind of a change did the glass undergo?

#### **Experiment 4.—Physical and Chemical Change.** *Materials:* Copper wire, magnesium, sulphur.

(a) Examine a piece of copper wire and notice especially its color. Grasp one end of the wire with the forceps, and hold the other end in

## Experiments.

the flame until the copper melts and undergoes a definite change. Then remove it from the flame and examine the product. Compare its properties with those of the copper. Is it apparently a different substance from the copper? Why? What kind of a change did the melted copper undergo?

(b) Examine a piece of magnesium ribbon and note its properties, especially the color, luster, and flexibility. Record these properties. Then grasp one end of the magnesium with the forceps and hold the other end for an instant in the Bunsen flame. Observe the result. Record it. Examine the product and compare its properties with those of the original substance. Has the essential change in the magnesium been physical or chemical? Why?

(c) Examine a piece of roll sulphur and note its properties, *e.g.* color, brittleness, solid condition, etc. Put a very small piece upon a block of wood and light it by directing the flame of the Bunsen burner upon it. Observe the color and size of the flame of the burning sulphur. Observe also (cautiously) the odor of the gaseous product by wafting a little gently toward the nose. Compare the properties of this substance with those of the sulphur. Has the sulphur undergone a physical or chemical change? Why?

### ANSWER :

(1) What are the evidences of chemical changes in this experiment?

(2) If a known weight of copper had been consumed in (a), could it have been recovered without loss?

## OXYGEN.

**Experiment 5.—Preparation of Oxygen.** *Materials:* 15 grams potassium chlorate, 15 grams manganese dioxide, 5 bottles (about 250 cubic centimeters each), filter paper, joss stick or splint of wood, sulphur, deflagrating spoon, piece of charcoal fastened to one end of a copper wire (30 centimeters long), wad of iron thread (often called "steel wool"). The *apparatus* is shown in Figure 102. *A* is a large test tube provided with a one-hole rubber stopper, to which is fitted a short glass tube, *B*; the delivery tube, *D*, is attached to the short glass tube by the rubber tube, *C*. (Directions for constructing and arranging the apparatus may be found in the Introduction, § 5.)

Weigh the potassium chlorate on a piece of paper creased lengthwise, and slip it into the test tube; do the same with the manganese dioxide. Shake the test tube until the chemicals are thoroughly mixed; then hold

the test tube in a horizontal position and roll or shake it until the mixture is spread along about one half of the tube. Insert the stopper with its tubes, and clamp the test tube to the iron stand, as shown in the

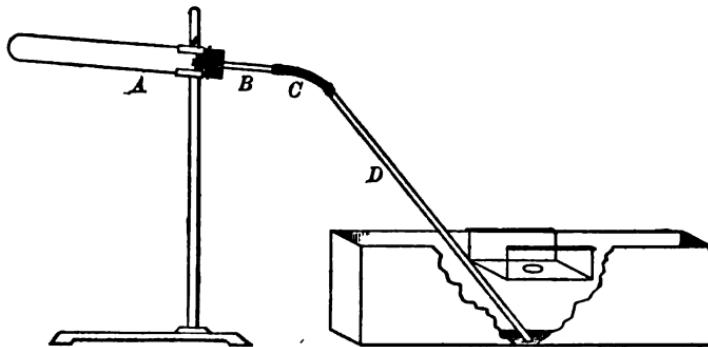


FIG. 102.—Apparatus arranged for preparing oxygen.

figure, taking care not to crush the tube; the test tube should incline toward the trough, to prevent moisture from flowing back upon the hot glass.

Fill the pneumatic trough with water until the shelf is just covered. Fill the bottles *full* of water, cover each with a piece of filter paper, invert them in the trough, and remove the filter paper; leave two bottles on the shelf and three on the bottom. The end of the delivery tube should rest on the bottom of the trough, just under the hole in the shelf.

Heat the whole test tube gently with a flame about 8 centimeters (or 3 inches) high. When the gas bubbles regularly through the water, slip a bottle over the hole. The gas will rise in the bottle and force out the water. Move the flame slowly along the test tube, but concentrate the heat toward the closed end, and always keep the flame behind any water which may be driven out of the mixture. If the gas is evolved too rapidly, lessen the heat; if too slowly, increase it; if not at all, examine the stopper and the rubber connecting tube for leaks, and adjust accordingly. When the first bottle of gas is full, remove and cover it with a piece of wet filter paper, and slip another bottle over the hole. When five bottles of gas have been collected, remove the end of the delivery tube from the water, lest the cold water be drawn up into the hot test tube as the gas contracts.

Perform the next experiment at once.

**Experiment 6.—Properties of Oxygen.**

Proceed as follows with the oxygen prepared in the preceding experiment.

(a) Dip a glowing joss stick into one bottle, and observe the change. Remove the stick, and repeat as many times as possible. Does the gas burn? How does the glowing stick change? What property of oxygen does this experiment show?

(b) Put a small piece of sulphur in the deflagrating spoon, hold the spoon in the flame until the blue flame of the burning sulphur can be seen, then lower the spoon into a bottle of oxygen. Notice the change in the flame. Describe it. Brush a little of the vapor *cautiously* toward the nose. Of what does the odor remind you? (Plunge the spoon into water to extinguish the burning sulphur, and cover the bottle with a piece of filter paper.)

(c) Hold the charcoal in the flame long enough to produce a faint glow, then lower it into a bottle of oxygen. Describe the result.

(d) Twist one end of the copper wire (used in (c)) around the wad of iron thread, heat the end an instant in the flame, and quickly lower it into a bottle of oxygen. The iron thread should burn brilliantly. If it does not, heat it a second time in the flame, and lower it again into the bottle of oxygen. Describe the result.

(e) With the remaining bottle, repeat any of the above experiments.

**EXERCISES:**

(1) Write a brief account of the above experiments in your note book, answering all questions and directions.

(2) Sketch the apparatus used to prepare oxygen.

(3) Summarize the properties of oxygen.

(4) What is its most characteristic property?

(NOTE.—The test tube used in Experiment 5 may be cleaned with warm water.)

**Experiment 7.—Preparation of Oxygen from Mercuric Oxide.**

*Materials:* Mercuric oxide, stick of wood.

Put a little mercuric oxide on the end of a narrow piece of paper creased lengthwise, and slip the powder into a test tube. The powder should nearly fill the round end of the test tube. Hold the test tube in a horizontal position, shake it to spread the powder into a thin

layer, attach the test-tube holder, and heat the test tube (still horizontal) in the upper part of the Bunsen flame. Do not heat one place, but move the tube back and forth. As soon as a definite change is noticed inside the tube, insert a glowing joss stick. Observe and describe the change. If there is no change, heat strongly, and test again. What gas is liberated? Observe the deposit inside the tube. What is it? If its nature is doubtful, let the tube cool, and examine again.

**EXERCISES:**

- (1) Describe briefly the whole experiment.
- (2) What historical interest has this experiment?

(NOTE.—If the test tube has been partially melted, save it for a subsequent experiment.)

### HYDROGEN.

**Experiment 8.—Preparation of Hydrogen.** *Materials:* Granulated zinc, dilute sulphuric acid, pneumatic trough, four bottles, filter paper, taper, matches. The apparatus is shown in Figure 103. *A* is a large test tube provided with a two-hole stopper, through which passes the safety tube, *B*, and the right-angle bend, *C*; the long (15 cm. or 6 in.) delivery tube, *E*, is attached to the bent tube by the rubber tube, *D*.

The safety tube may be advantageously replaced by the dropping tube described in Experiment 96.

Fill the test tube half full of granulated zinc as follows: Crease a piece of paper lengthwise, pour the zinc from the bottle upon the paper, incline the test tube, and slip the zinc into it from the paper—do not drop it in. Insert the stopper with its tubes; if the end of the safety tube does not go in easily, hold the test tube in a horizontal position and shake the zinc about, and at the same time push the stopper gently but firmly into place. Clamp the apparatus into the position shown in the figure or stand it in a test-tube rack.

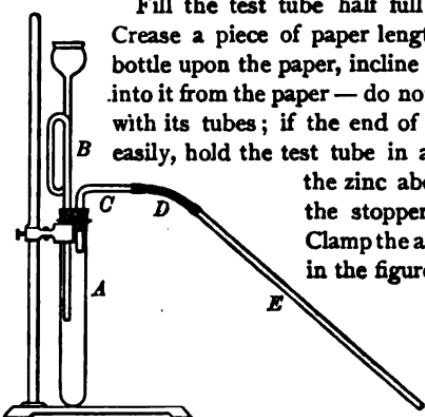


FIG. 103.—Apparatus for preparing hydrogen.

Fill the pneumatic trough with water as before, and adjust the apparatus so that the end of the delivery tube rests on the bottom of the trough under the hole in the shelf.

Fill the bottles with water and invert them in the trough, as in Experiment 5.

## Experiments.

Pour enough dilute sulphuric acid through the safety tube to fill the test tube about half full, taking care to leave a little acid in the lower bend of the safety tube. This precaution prevents the gas from escaping from the back of the apparatus; if at any time the gas should flow backward, pour a little acid into the bend; if the acid does not flow down the safety tube, loosen the stopper for an instant. As soon as the interaction of the zinc and sulphuric acid produces hydrogen, the gas will bubble freely through the water in the trough. Slip a bottle over the hole, and collect and remove the bottle of gas as in Experiment 5, taking care to cover the bottle firmly with a piece of wet filter paper. If the evolution of gas slackens or ceases, add a little more acid through the safety tube. Collect four bottles of hydrogen, and proceed at once with the next experiment.

### Experiment 9.—Properties of Hydrogen.

Study as follows the hydrogen gas prepared above:—

- (a) Uncover a bottle for an instant to let a little air in, and then drop a lighted match into the bottle. Describe the result.
- (b) Remove the paper from a bottle of hydrogen, and allow it to remain uncovered for three minutes—by the clock. Then show the presence or absence of hydrogen by dropping a lighted match into the bottle. Describe the result. What property of hydrogen is shown by this experiment?
- (c) Verify your answer to the last question, thus: Hold a bottle of air over a covered bottle of hydrogen, remove the paper, and bring the mouths of the bottles close together. (See Fig. 1.) Hold them there for a minute or two, then stand the bottles on the desk and cover them with wet filter paper. Drop a lighted match into each bottle. What has become of the hydrogen? How does (c) verify (b)?
- (d) Invert a covered bottle of hydrogen, remove the paper, and quickly thrust a lighted taper up into the bottle. Withdraw the taper and then insert it again. Does the hydrogen burn? If so, where? Does the taper burn when in the bottle? When out of the bottle? Feel of the neck of the bottle; describe and explain. What *three* properties of hydrogen are shown by this experiment?

### Experiment 10.—Burning Hydrogen. (Teacher's Experiment.)

**Materials:** Apparatus shown in Figure 2, which consists of a

500 cubic centimeter flask fitted with a two-hole rubber stopper, dropping tube, and double right-angle bend; the last is attached to a U-tube, which is also connected to a delivery tube provided with a short piece of tight rubber tubing; calcium chloride, small bottle, platinum wire, cotton, granulated zinc, dilute sulphuric acid.

Fill the U-tube two thirds full of calcium chloride, put a wad of cotton beneath the stopper of each arm, and connect the U-tube with the generator and the delivery tube.

Stand the apparatus on the table, examine all joints to be sure they are tight, extinguish all flames in the vicinity, and proceed exactly according to the following directions:—

Pour slowly but continuously through the dropping tube enough (about 50 cubic centimeters) dilute sulphuric acid upon at least 25 grams of granulated zinc to produce a steady current of hydrogen gas for about five minutes. It is advisable to use considerable zinc and a moderate amount of acid. Acid may be added slowly after the evolution of gas begins, but, of course, no air should be introduced. Let the gas bubble through the acid for at least *two minutes* by actual observation, then attach the platinum tip and the rubber connector to the end of the delivery tube, leaving a short space between the ends of the two glass tubes so that the rubber tube may be compressed suddenly, if necessary. Let the gas run for *another full minute*. This latter precaution is to drive all air out of the platinum tube. Light the hydrogen, and observe *at once* the nature of the flame, its color, heat (by holding a match or platinum wire over it), and any other striking property. Then hold a small dry bottle over the flame in such a position that the flame is just inside the bottle. When conclusive evidence of the product of burning hydrogen is seen inside the bottle, remove the bottle, and extinguish the flame *at once* by pinching the rubber connector. Remove the generator to the hood, and if the evolution of hydrogen is still brisk, dilute the acid by pouring water through the dropping tube. Examine the inside of the bottle. What is the deposit? Explain its formation.

#### EXERCISES FOR THE CLASS:

- (1) What does this experiment suggest about the composition of water?
- (2) Does this experiment illustrate oxidation? Why? Synthesis? Why?
- (3) Describe the whole experiment, and sketch the apparatus.

## Experiments.

### WATER.

**Experiment 11.—General Distribution of Water.** *Materials:* Wood, meat, potato.

Heat successively in dry test tubes a small piece of wood, of meat, or of potato (or any other fresh vegetable). Hold the open end of the test tube lower than the other end. Is there conclusive evidence of water? Since most animal and vegetable substances act similarly, what general conclusion can be drawn from this experiment?

**Experiment 12.—Simple Tests for Impurities in Water.** *Materials:* Distilled water, impure water (containing organic matter, a sulphate, a chloride, and a lime compound); nitric acid, acetic acid, sulphuric acid (concentrated), solutions of potassium permanganate, silver nitrate, barium chloride, ammonium oxalate; and lime-water.

(a) *Organic Matter.* Fill a test tube half full of the impure water, add a drop or two of concentrated sulphuric acid, and sufficient potassium permanganate solution to color the water a light purple. Stir the mixture until the color is uniform. Hold the test tube in the holder and heat the solution gently and cautiously to the boiling point, taking care to prevent the liquid from jumping out of the test tube. The organic matter is oxidized by the potassium permanganate and the solution becomes brown or colorless. Apply this test to distilled water, to faucet water, and to water containing bits of paper. State the result.

(b) *Chlorides.* To a test tube half full of distilled water add a few drops of nitric acid, and then a few drops of silver nitrate solution. Do the same with the impure water (which contains a chloride). What is the difference between the results? The cloudiness, or solid, is due to silver chloride, which is always formed when silver nitrate is added to hydrochloric acid or a chloride in solution (chlorides being closely related to hydrochloric acid). Silver chloride is soluble in ammonium hydroxide. Its formation is the usual test for chlorides. Apply this test to faucet water, and state the result.

(c) *Sulphates.* To a test tube half full of the impure water add a few drops of barium chloride solution. The white precipitate is barium sulphate. It is insoluble in all common liquids, and is always formed when barium chloride is added to sulphuric acid or a sulphate in solution (sulphates being closely related to sulphuric acid). Test faucet water for sulphates, and state the result.

(d) *Lime Compounds.* Add a few drops of an ammonium oxalate solution to a test tube half full of the impure water. A white precipitate will be formed. It is calcium oxalate, and is soluble in hydrochloric acid. This is the usual test for calcium compounds, which are often called lime compounds, because the well-known substance lime is calcium oxide. Apply this test to faucet water, and state the result.

**Experiment 12 a.—Testing Unknown Substances.** Procure several substances, dissolve each in water, and test portions of the clear solution for a chloride, a sulphate, and a lime compound. Record the results.

**Experiment 13.—Distillation. (Teacher's Experiment.) Materials:** Condenser, etc., shown in Figure 6, potassium permanganate, impure water, and solutions used in Experiment 12.

Fill the flask, *C*, half full of water known to contain the impurities mentioned in Experiment 12, add a few crystals (3 or 4) of potassium permanganate, and connect with the condenser as shown in Figure 6. Attach the inlet tube to the faucet, fill the condenser slowly, and regulate the current so that a small stream flows continuously from the outlet tube into the sink or waste pipe. Heat the liquid in *C* gradually, and when it boils, regulate the heat so that the boiling is not too violent. As the distillate collects in the receiver, *D*, test separate portions for organic matter, chlorides, sulphates, and calcium compounds.

#### EXERCISES FOR THE CLASS :

- (1) Is organic matter found ?
- (2) Is mineral matter found ?
- (3) If the distilling liquid had contained a volatile substance, like ammonia or alcohol, would the distillate contain such a substance ?

#### Experiment 14.—Solubility of Gases.

(a) Warm a little faucet water in a test tube. What is the *immediate* evidence of a previously dissolved gas ? Is there evidence of much gas ? What effect has increased heat upon the dissolved gas ?

(b) Warm slightly a few cubic centimeters of ammonium hydroxide in a test tube. Do the results resemble those in (a) ? As soon as the final result is obtained, pour the remaining liquid down the sink and flush well with water.

**Experiments.**

(c) Repeat (b), using a little concentrated hydrochloric acid. Do the results resemble those of (a) and (b) ?

**ANSWER :**

- (1) How does increased temperature affect the solubility of gases ?
- (2) What gases dissolve freely in water ?

**Experiment 15.—Solubility of Liquids.** *Materials:* Alcohol, kerosene, glycerine, carbon disulphide.

(a) To a test tube half full of water add a little alcohol and shake. Is there evidence of solution ? Add a little more and shake. Add a third portion. Is there still evidence of solution ? Draw a conclusion as to the solubility of alcohol in water.

(b) Repeat (a), using successively kerosene, glycerine, and carbon disulphide. Observe the results and conclude accordingly.

(c) Summarize the results in a table.

**Experiment 16.—Solubility of Solids.** *Materials:* About 20 grams of powdered copper sulphate, 6 grams of powdered potassium chlorate, 1 gram of calcium sulphate.

(a) Label three test tubes I, II, III. Put 10 cc. of water into each. To I add 1 gram of powdered copper sulphate, to II add 1 gram of powdered potassium chlorate, to III add 1 gram of calcium sulphate. Shake each test tube, and then allow them to stand undisturbed for a few minutes. Is there evidence of solubility in each case ? Is there evidence of a varying degree of solubility ? If III is doubtful, carefully transfer a portion of the *clear* liquid to an evaporating dish by pouring it down a glass rod (see Introduction, § 6 (1) (a)), and evaporate to dryness. Is there now conclusive evidence of solution ? Draw a general conclusion from this experiment. Save solutions I and II for (b).

Tabulate the results of (a) as follows, using the customary terms to express the degree of solubility :—

**TABLE OF SOLUBILITY OF TYPICAL SOLIDS.**

SOLUTE.	SOLVENT.	RESULT.
1. Copper sulphate	Water at tempera-	1.
2. Potassium chlorate	ture of labora-	2.
3. Calcium sulphate	tory.	3.

(b) Heat I and add gradually 4 more grams of powdered copper sulphate. Does it all dissolve? Heat II and add 4 more grams of powdered potassium chlorate. Does it all, or most all, dissolve? What general effect has increased heat on the solubility of solids? What is the difference between this general result and that in Experiment 14? Save the solutions for (c).

(c) Heat I and II nearly to boiling, and as the temperature increases add the respective solids. Do not boil the solution; keep it near the boiling point by frequent heating. Is there a limit to their solubility? Draw a general conclusion from these typical results.

**Experiment 17.—Supersaturation.** *Material:* Sodium thiosulphate.

Fill a test tube nearly full of crystallized sodium thiosulphate and add two or three cubic centimeters of water. Warm slowly. As solution occurs, heat gradually to boiling. Pour the solution into a warm, clean, dry test tube, cover the test tube, and let it stand undisturbed until cool. Then drop in a small crystal of sodium thiosulphate and watch for any simple but definite change. What happens? Is the excess of solid large? How does a supersaturated solution differ from a saturated one?

**Experiment 18.—Water of Crystallization.** *Materials:* Crystallized sodium carbonate, gypsum, copper sulphate, evaporating dish, gauze-covered ring (or tripod).

(a) Heat a few small crystals of sodium carbonate in a dry test tube, inclining the test tube so that the open end is the lower. What is the evidence that they contained water of crystallization? If there is any marked change in the appearance of the crystals, describe and explain it.

(b) Repeat, using a crystal of gypsum. Answer the question asked in (a).

(c) Heat two or three small crystals of copper sulphate in an evaporating dish which stands on a gauze-covered ring. As the action proceeds, hold a dry funnel or glass plate over the dish. Is there conclusive evidence of escaping water of crystallization? Do the crystals change in color? In shape? Can the form of the crystals be changed by gently touching the mass with a glass rod? Continue to heat until the resulting mass is a bluish gray. Let the dish cool. Meanwhile heat a test tube one half full of water. When the dish has cooled somewhat,

## Experiments.

pour the hot water slowly into the dish upon the copper sulphate. Explain the change in color, if any. If there are any lumps, crush them with a glass rod. Let the clear solution evaporate for several hours. Are crystals deposited? If not, heat a few minutes, and cool again. If so, why? Have they water of crystallization, and, if so, where did they get it?

### Experiment 19.—Efflorescence.

Put a fresh crystal of sodium carbonate and of sodium sulphate on a piece of filter paper, and leave them exposed to the air for an hour or more. Describe any marked change. What does this change show about the air? About the crystal?

### Experiment 20.—Deliquescence.

Put on a glass plate or block of wood a small piece of granulated calcium chloride and of sodium hydroxide. Leave them exposed to the air for an hour or more. Describe any marked change which takes place. Compare the action with that of Experiment 19.

**Experiment 21.—Solution and Chemical Action.** *Materials:* Powdered tartaric acid, sodium bicarbonate, lead nitrate, potassium dichromate, mortar, dish of water.

(a) Mix in a dry mortar small but equal amounts of powdered tartaric acid and sodium bicarbonate. Is there any decided evidence of chemical action? Pour the mixture into a dish of water. Is there conclusive evidence of chemical action?

(b) Repeat, using powdered lead nitrate and powdered potassium dichromate.

Describe the results in (a) and (b). How does solution influence chemical action? Why are so many solutions used in the laboratory?

**Experiment 22.—Electrolysis of Water.** (*Teacher's Experiment.*) *Materials:* Hofmann apparatus, sulphuric acid, taper, matches, short piece of capillary glass tubing.

Fill the Hofmann apparatus, Figure 10, with water containing 10 per cent of sulphuric acid, so that the water in the reservoir tube stands a short distance above the gas tubes after the stopcock in each has been closed. Connect the platinum terminal wires with a battery of at least two cells. As the action proceeds, small bubbles of gas rise and collect

at the top of each tube. Allow the current to operate until the smaller volume of gas is from 8 to 10 centimeters in height. Measure the height of each gas column. Assuming that the tubes have the same diameter, the volumes are in approximately the same ratio as their heights. How do the volumes compare?

Test the gases as follows: (a) Hold a glowing taper over the tube containing the smaller quantity of gas, cautiously open the stopcock to allow the water (or air) to run out of the glass tip, and then let out a little gas upon the glowing taper. What is the gas? Repeat until the gas is exhausted. Care must be taken not to lose the gas. It is advisable to have at hand several partially burned tapers or thin splints, in case any escaping water extinguishes the first one. (b) Open the other stopcock long enough to force out the water in the glass tip; close the stopcock, and, by means of a short rubber tube, attach the capillary tube close to the end of the glass tip. Open the stopcock again, let out the gas slowly, and hold at the same time a lighted match at the end of the tip, then immediately thrust a taper into the small and almost colorless flame. What is the gas? Repeat until the gas is exhausted.

**EXERCISES FOR THE CLASS:**

- (1) Describe the whole experiment.
- (2) Draw a general conclusion from this experiment.
- (3) What does this experiment show about the composition of water?
- (4) Sketch the apparatus.

**Experiment 23.—Interaction of Water and Chlorine. (Teacher's Experiment.)** *Materials:* Glass tube 1 meter long and about 2 centimeters in diameter, cork for one end, evaporating dish, chlorine water.

Construct a chlorine generator, as described in Experiment 38, and prepare about 250 cubic centimeters of chlorine water by causing the gas to bubble through a bottle of water until the water smells strongly of the gas. Close one end of the tube with a cork. The cork must fit air tight, and as a precaution should be smeared (after insertion) with vaseline or coated with paraffin. Fill the tube full of chlorine water, cover the open end with the thumb or finger, invert the tube, and immerse the open end in the evaporating dish, which should be nearly

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full of chlorine water. Clamp the tube in an upright position, and stand the whole apparatus where it will receive the direct sunlight for at least six hours. Bubbles of gas will soon appear, rise, and collect at the top. When sufficient gas for a test has collected, unclamp the tube, cover the open end with the thumb or finger, invert the tube, and put a glowing taper into the gas. Repeat as long as any of the gas remains.

### EXERCISES FOR THE CLASS:

- (1) What gas is produced by the interaction of chlorine and water?
- (2) Describe this experiment.
- (3) What does it show about the composition of water?
- (4) Sketch the apparatus.

**Experiment 24.—Interaction of Water and Sodium.** *Materials:* Sodium, pneumatic trough filled with water as usual, tea lead, forceps, red litmus paper.

**Precaution.** Sodium should be handled cautiously and used strictly according to directions. Small fragments must not be left about nor thrown into the refuse jar, but into a large vessel of water especially provided for that purpose.

(a) If the sodium is brown, scrape off the coating. Cut off a piece of sodium not larger than a small pea, and drop it upon the water in the trough. Stand far enough away so that you can just see the action. Wait until you are sure the action has stopped, and then describe all you have seen.

(b) The action in (a) may be further studied as follows: Fill a test tube with water, invert it, and clamp it in the trough so that the mouth is over the hole in the shelf of the trough. Wrap a small piece of sodium loosely in a piece of tea lead about 5 centimeters (2 inches) square, make two or three small holes in the tea lead, and then thrust it under the shelf of the trough with the forceps. A gas will rise into the test tube. Proceed similarly with additional small pieces of sodium and dry tea lead until the test tube is nearly full of gas; then unclamp and remove, still keeping the tube inverted. Hold a lighted match, for an instant, at the mouth of the tube. Observe the result, watching especially the mouth of the tube. What is the gas? Why? Remembering that sodium is an element, where must the gas have come from? If there is any doubt about the nature of the gas, collect more, and subject it to those tests which will prove its nature.

(c) Put a piece of filter paper on the water in the trough, and before it sinks drop a small piece of sodium upon it. Stand back and observe the result. Wait for the slight explosion which usually occurs soon after the action stops. Describe all you have seen. What burned? What caused it to burn? To what is the vivid color probably due?

(d) Test the water in the trough with red litmus paper. Push the paper to the bottom or to the place where it is certain that chemical action between water and sodium has taken place. Test until the red litmus paper has undergone a decided change in color. Describe this final result. With another piece of red litmus paper test a solution of sodium hydroxide. Is the result similar? Dip a glass rod or the platinum test wire (see Int. § 5 (4)) into this solution and hold it in the Bunsen flame. Describe the result. The color is due to sodium. Is the color of this flame and that noticed in (c) the same? Are the dissolved substances probably identical?

(e) What does the whole experiment show about the composition of water?

### THE AIR.

**Experiment 25.—Composition of the Air.** *Materials:* Solutions of pyrogallic acid and potassium hydroxide,<sup>1</sup> pneumatic trough half filled with water, 500 and 25 cubic centimeter graduated cylinders. The *apparatus* (Fig. 103 a) consists of a bottle holding 250 cubic centimeters provided with a one-hole rubber stopper through which passes a short glass tube closed at both ends and projecting 5 centimeters (2 inches) above the stopper.

(a) The volume of the bottle is found thus: Fill the bottle full of water from the pneumatic trough. Push the stopper into the bottle as far as it will go, and then insert the glass tube. Remove the stopper. Pour most of the water from the bottle into the 500 cubic centimeter graduate, and read the volume: the last portions of the water in the bottle should be poured into the 25 cubic centimeter graduate, so that the volume can be read accurately. (See Fig. 101.) Record the total volume of the flask as shown in (d).



FIG. 103 a.  
—Apparatus  
for determin-  
ing oxygen in  
air.

<sup>1</sup> The pyrogallic acid is a 10 per cent solution, and the potassium hydroxide 50 per cent.

## Experiments.

(b) Measure exactly 10 cubic centimeters of pyrogallic acid in the small graduate (see Int. § 6 (3) (d)), and pour it into the bottle. Add 20 cubic centimeters of potassium hydroxide solution, insert the rubber stopper quickly, and then push the glass tube through the stopper until the inner end is level with the inner surface of the stopper. Shake the bottle vigorously at intervals from twenty to twenty-five minutes. During this operation the oxygen is absorbed by the solution.

(c) Place the bottle on its side in the water of the pneumatic trough, inclining it slightly so that the lower edge of the bottle rests upon the bottom of the trough and the hole in the stopper is just beneath the surface of the water; gradually pull out the tube, taking care (1) not to let any of the solution run out, (2) not to let too much water run in, and (3) to keep the hole in the stopper constantly below the surface. After the water has stopped running in, insert the tube, remove the bottle, and measure carefully the volume of the final liquid in the bottle.

(d) Record and calculate as follows:—

(a) Volume of original solution	= 30 cc.
(b) Capacity of flask	= cc.
(c) Volume of air taken ( $b - a$ )	=
(d) Final volume of liquid	=
(e) Volume of water which entered ( $d - a$ )	=
(f) Per cent of water which entered ( $e + c$ )	=

But the per cent of entering water equals the per cent of gas absorbed, hence

(g) Per cent of oxygen	=
(h) Per cent of nitrogen ( $100 - g$ )	=

### **Experiment 26.—Air contains Water Vapor.**

Place a piece of sodium hydroxide upon a glass plate and let it remain exposed to the air fifteen minutes or more. Describe the result? What does the result show about the air?

### **Experiment 27.—Air contains Carbon Dioxide.**

(a) Expose a small bottle of limewater to the air. After a short time, examine the surface of the liquid. Describe the change. Explain it.

(b) If a blast lamp (or bicycle pump) is available, replace the lamp with a glass tube, and force air through a bottle half full of limewater, until a definite change occurs. Describe it. Explain it.

### ACIDS, BASES, AND SALTS.

**Experiment 28.—General Properties of Acids.** *Materials:* Dilute sulphuric, nitric, and hydrochloric acids, glass rod, litmus paper (both colors), zinc.

Fill separate test tubes one third full of each of the acids. Label the tubes in some distinguishing manner.

(a) Dip a clean glass rod into each acid and *cautiously* taste it. Describe the taste by a single word.

(b) Dip a clean glass rod into each acid and put a drop on both kinds of litmus paper. The striking change is characteristic of acids; draw a general conclusion from it.

(c) Slip a small piece of zinc into each test tube successively. If no chemical action results, warm gently. Test the most obvious product by holding a lighted match inside of each tube. What gas comes from the hydrochloric and sulphuric acids?

(d) Summarize the general results of this experiment.

**Experiment 29.—General Properties of Bases.** *Materials:* Litmus paper (both colors), glass rod, sodium hydroxide and potassium hydroxide solutions, and ammonium hydroxide.

(a) Rub a little of each liquid between the fingers, and describe the feeling. *Cautiously* taste each liquid by touching to the tip of the tongue a rod moistened in each, and describe the result.

(b) Test each solution with litmus paper. Describe the result.

(c) Summarize the general results of this experiment.

(d) Compare acids and bases as to taste and to reaction with litmus.

**Experiment 30.—Properties of Different Salts.** *Materials:* Litmus paper (both colors), glass rod, dilute solutions of sodium chloride, potassium nitrate, potassium sulphate, acid sodium sulphate, sodium carbonate, potassium carbonate, alum, and barium chloride.

Test each solution with litmus paper. Describe the result. Compare with the litmus reaction of acids and bases.

Draw a conclusion from this experiment.

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**Experiment 31. — The Nature of Common Substances.**

Determine by the litmus test the nature of lemon juice, vinegar, sweet and sour milk, washing soda, borax, wood ashes, faucet water, baking soda, sugar, cream of tartar, the juice of any ripe fruit and any unripe fruit.

Make a solution of each of the solids before testing. Tabulate the results as follows:—

NATURE OF COMMON SUBSTANCES.

ACID	ALKALINE.	NEUTRAL

**Experiment 32. — Neutralization.** *Materials:* Sodium hydroxide (solid), hydrochloric acid, nitric acid, silver nitrate solution, blue litmus paper, glass rod, evaporating dish, gauze-covered ring.

Dissolve a small piece of sodium hydroxide in an evaporating dish half full of water. Slowly add dilute hydrochloric acid, until a drop taken from the dish upon a glass rod reddens blue litmus paper. Then evaporate to dryness by heating over a piece of wire gauze supported by a ring. Since the residue mechanically holds traces of the excess of hydrochloric acid added, it is necessary to remove this acid before applying any test. Heat the dish until all the yellow color disappears, then moisten the residue carefully with a few drops of warm water and heat again to remove the last traces of acid. This precaution is essential to the success of the experiment.

Test a portion of the residue with litmus paper to find whether it has acid, alkaline, or neutral properties. Taste a little. Test (*a*) a solution of the residue for a chloride, and (*b*) a portion of the solid residue for sodium by the flame test. (See Exps. 12 (*b*) and 24 (*d*)). Draw a definite conclusion from the total evidence.

**HEAT, LIGHT, ELECTRICITY, AND CHEMICAL ACTION.**

**Experiment 33.—Heat and Chemical Action.** *Materials:* Lime, evaporating dish, match.

Put a large piece of lime in an evaporating dish, and sprinkle a little water over it. Watch for a change. If no marked change soon occurs, add a little more water. Describe the change as soon as there is evidence of much heat. What caused the heat?

**Experiment 34.—Heat and Chemical Action.** *Materials:* Sulphur, powdered iron, dilute hydrochloric acid.

Put about 3 grams of sulphur and 3 grams of powdered iron in a test tube. Cover the mouth of the test tube with the thumb and shake until the two substances are well mixed. Attach the test tube to the holder and heat strongly in the flame. As soon as the sulphur melts and boils and the contents give evidence of decided chemical action, remove the test tube at once from the flame, and watch the change. Is there evidence of heat? Of increasing heat? Of much heat?

When the tube is cool, break the end, and examine the contents. Describe it. It is a compound called iron sulphide, and is the product of the chemical action which was started by heat. But the chemical action itself was so vigorous that it increased the heat.

The fact that the product differs from the original mixture may be shown as follows: Add dilute hydrochloric acid to a part of the product and also to a little of the original mixture, testing the gaseous product in each case by the odor. Is the odor the same?

State briefly how heat and chemical action are related, using this experiment as an illustration.

**Experiment 35.—Light and Chemical Action.** *Materials:* Potassium bromide, silver nitrate solution, funnel, filter paper, glass rod.

Dissolve a very little potassium bromide in a test tube one fourth full of water, add an equal volume of silver nitrate solution, and shake. The precipitate is silver bromide. Describe it. Filter (see Int. § 4). Remove the filter paper from the funnel, unfold it, and expose the silver bromide for a few minutes to the light—sunlight, if possible. Describe the change. What caused the change? How is this property of silver bromide utilized?

## Experiments.

**Experiment 36.—Electricity and Chemical Action. (Teacher's Experiment.)**

Repeat Experiment 22.

**EXERCISES FOR THE CLASS:**

- (1) Define electrolysis, electrode, electrolyte, ion, anion, cation.
- (2) State briefly the accepted explanation of the electrolysis of water.
- (3) Is hydrogen an anion or cation? At what electrode does it collect?
- (4) Answer the same questions (as in 3) about oxygen.

**Experiment 37.—Electricity and Chemical Action. (Teacher's Experiment.)** *Materials:* Starch, potassium iodide, mortar and pestle, filter paper, sheet tin (or iron), battery of two or more cells.

Grind together in a mortar a lump of starch and a crystal of potassium iodide. Add enough water to make a thin liquid. Dip a strip of filter paper into the mixture, and spread the wet paper upon a sheet of tin (or iron). Press the end of the wire attached to the zinc (of the battery) upon the tin, and draw the other wire across the sheet of paper. The marks are caused by iodine which is liberated from the potassium iodide and colors the starch.

**EXERCISES FOR THE CLASS:**

- (1) Describe briefly this experiment.
- (2) Iodine is a non-metal. At what electrode is it liberated? Is iodine an anion or a cation?

### CHLORINE.

*(Perform this experiment in the hood.)*

**Experiment 38.—Preparation of Chlorine.** *Materials:* Concentrated hydrochloric acid, 30 grams manganese dioxide, wad of fine iron thread, cotton, calico, paper with writing in lead pencil and in ink, litmus papers (both colors), taper. The *apparatus* is shown in Figure 104 (though a dropping tube may replace B, as in Exp. 96); and there are also needed four bottles, a wooden block (about 10 centimeters or 4 inches square) with a hole in the center, four glass plates to cover the bottles, and a piece of copper wire 15 centimeters long.

Weigh the manganese dioxide upon a piece of paper creased lengthwise. Slip it into the test tube, A (see Int. § 6 (c)). Arrange the appa-

ratus as shown in the figure. Pour enough concentrated hydrochloric acid through the safety tube to cover the manganese dioxide. Heat gently with a small flame, keeping the flame below the level of the contents of the test tube. Chlorine is rapidly evolved as a greenish gas, and passes into the bottle, *G*, which should be removed when full (as seen by the green color) and covered with a glass plate; the bottle may be easily removed by holding the block, *F*, in one hand and pulling the bottle, *G*, aside, bending the whole delivery tube at the same time at the rubber connection, *D*. If the evolution of gas slackens, add more acid through the safety tube. Collect four bottles, and perform the next experiment at once.

#### Experiment 39.—Properties of Chlorine.

Study as follows the gas prepared above:—

(a) Twist one end of a copper wire around a wad of iron thread, heat it, and thrust it into a bottle of chlorine. Describe the result.



FIG. 105.—Wads of cotton and iron.

(b) Into a bottle of dry chlorine put a piece of calico, litmus paper (both colors), and paper containing writing in black and in red ink. Allow the whole to remain undisturbed for a few minutes and then describe the change, if any. Add several drops of water, and describe the change. Draw a general conclusion from the whole experiment.

(c) Hold a burning taper in a bottle of chlorine long enough to observe the result. Draw a conclusion. Verify it thus: Twist the other end of the copper wire around a piece of cotton, as shown in Figure 105; cautiously heat<sup>1</sup> about 10 cubic centimeters of turpentine in a large test tube; saturate

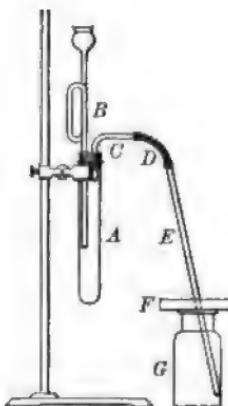


FIG. 104.—Apparatus arranged for preparing chlorine.

<sup>1</sup> Hold the test tube with the holder. Remember that turpentine ignites easily. If the turpentine catches fire, press a damp towel over it.

## Experiments.

the cotton with the hot turpentine and lower it into a bottle of chlorine. Describe the result. When the action is over, examine the cotton, and draw a conclusion regarding the action between hot turpentine and chlorine.

Wax (in the taper) and turpentine are mainly compounds of hydrogen and carbon. Explain the result in (c).

**ANSWER :**

- (1) Many metals act like the iron in (a). What general conclusion can be drawn about the reaction of chlorine and metals?
- (2) What is essential for the bleaching action of chlorine?
- (3) What does (c) show about the attraction between chlorine and hydrogen?
- (4) What class of chemical changes is illustrated by (a)? What classes by (c)?
- (5) What class of chemical changes is illustrated by the preparation of chlorine?
- (6) What three striking properties has chlorine? How can it be distinguished from all gases previously studied?

**Experiment 40.—Bleaching by Bleaching Powder.** *Materials:* Bleaching powder, sulphuric acid, colored cloth.

Put a little bleaching powder into a test tube and add enough water to make a thin paste. Add a few drops of dilute sulphuric acid, and then dip several pieces of colored cloth into the mixture. Remove the cloth in a few minutes, and wash it with water. Describe the change in the cloth.

**Experiment 41.—Preparation of Hydrochloric Acid.** *Materials:* The *apparatus* used in Experiment 38; 20 grams sodium chloride, concentrated sulphuric acid, joss stick, litmus paper (blue), ammonium hydroxide. (*Perform this experiment in the hood.*)

(a) Put 8 cubic centimeters of water in a small bottle or evaporating dish, cautiously add 12 cubic centimeters of concentrated sulphuric acid, and stir until the two are mixed. While this mixture is cooling, weigh the salt, slip it into the test tube, and then arrange the apparatus as shown in Figure 104. Pour half the cold acid mixture through the safety tube, let it settle through the salt, and then add the remaining acid. Heat gently with a low flame, as in the preparation of chlorine. Hydrochloric acid gas is evolved, and passes into the bottle, which

should be removed when full, as directed under chlorine. A piece of moist blue litmus paper held at the mouth of the bottle will show when it is full. Collect these bottles, cover each with a glass plate, and set aside until needed.

(b) As soon as the third bottle of gas has been collected, removed, and covered, put in its place a bottle one fourth full of water. Adjust its height (if necessary) by wooden blocks so that the end of the delivery tube is just above the surface of the water. Continue to heat the generator at intervals, and the gas will be absorbed by the water. Shake the bottle occasionally.

Meanwhile study the gas already collected.

#### **Experiment 42.—Properties of Hydrochloric Acid Gas.**

Proceed as follows with the hydrochloric acid gas prepared by Experiment 41:—

(a) Insert a blazing joss stick into one bottle. Remove as soon as the change is noticed. Describe the change. Compare the action with the behavior of hydrogen and of oxygen under similar conditions.

(b) Hold a piece of wet filter paper near the mouth of the same bottle. Observe and describe the fumes. What is the cause?

(c) Invert a bottle, and stand it in a dish of water (*e.g.* the pneumatic trough). Describe any change noticed inside the bottle after a few minutes. What property of the gas does the result illustrate? Verify the observation by a simple test applied to the contents of the bottle.

(d) Drop into the remaining bottle of gas a piece of filter paper wet with ammonium hydroxide. Describe the result. What name has the product?

(e) State other properties of hydrochloric acid gas which you have observed; *e.g.* color, odor, density.

Proceed at once with the next experiment.

#### **Experiment 43.—Properties of Hydrochloric Acid.**

Remove the bottle in which the hydrochloric acid gas is being absorbed (see Exp. 41 (b)), and study the solution as follows:—

(a) Determine its general properties, *e.g.* taste (cautiously), action with litmus, and with magnesium.

(b) Add to a test tube half full of the hydrochloric acid a few drops of nitric acid and of silver nitrate solution. The white, curdy precipitate

is silver chloride. Filter part of the contents of the test tube, and expose the precipitate to the sunlight. Describe the change which soon occurs. To the remaining contents of the test tube add ammonium hydroxide, and shake. Describe the result.

**Experiment 44.—Tests for Hydrochloric Acid or a Chloride.**

(a) What is a simple test for hydrochloric acid gas or for concentrated hydrochloric acid?

(b) What is the usual test for hydrochloric acid?

(c) Dissolve a little sodium chloride in a test tube half full of water, and apply the test designated in (b). (Suggestions. See Exps. 12 (b) and 43 (b).)

**COMPOUNDS OF NITROGEN.**

**Experiment 45.—Preparation of Ammonia.** *Materials:* 15 grams lime, 15 grams ammonium chloride, 3 bottles, 2 glass plates, pneumatic trough filled as usual, litmus paper, stick of wood, filter paper.

The *apparatus* is shown (in part) in Figure 106. The large test tube, A, is provided with a one-hole rubber stopper to which is fitted the right-angle bend, C, connected with a short glass tube, B (12 centimeters or 5 inches long), by the rubber tube, D.

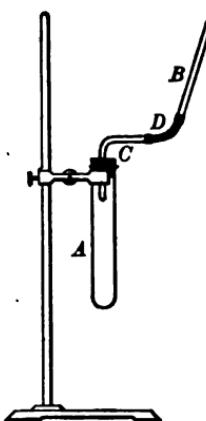


FIG. 106.—Apparatus for preparing and collecting ammonia gas.

(a) Weigh the lime and ammonium chloride separately, mix them thoroughly on a piece of paper, and slip the mixture into the test tube to which a little water has been previously added. Add a little water. Quickly insert the stopper with its tubes, and clamp the test tube as shown in the figure (taking care not to crush the test tube).

Slip the glass delivery tube, B, into a bottle, invert the bottle, and hold it so that the tube is in the position shown in the figure. Heat the test tube gently with a low flame, beginning near the top of the mixture and gradually working downward. Ammonia gas will pass up into the bottle, which should be removed when full and covered with a glass plate. A piece of moist red litmus paper held near the mouth will show when the bottle is full. *Do not smell at the mouth of the bottle.* Collect two bottles and set aside until needed.

(b) As soon as the last bottle has been collected, rearrange the apparatus to absorb the ammonia gas in water, as in the case of hydrochloric acid (see Exp. 41 (b)). Replace the short glass tube by the delivery tube, *E*, which should pass through the wooden block, *F*, into a bottle, *G*, one fourth full of water, so that the end is just above the surface of the water (see Fig. 104). Continue to heat the generator at intervals, and the gas will be absorbed by the water. Shake the bottle occasionally.

While the solution is being prepared, study the gas already collected.

#### Experiment 46.—Properties of Ammonia Gas.

Proceed as follows with the ammonia gas prepared in Experiment 45:—

(a) Test the gas in one bottle with moist litmus paper and with a blazing stick. Describe the result. Compare the action with the behavior of hydrogen, oxygen, and hydrochloric acid gas, under similar circumstances.

(b) Invert the same bottle and stand it upon the shelf of the pneumatic trough. Describe any change noticed inside the bottle. What property of the gas is revealed? Is it a marked property? Test the contents of the bottle with litmus paper (both colors).

(c) Pour a few drops of concentrated hydrochloric acid into an empty, warm, dry bottle. Roll the bottle until the inside is well coated. Cover it with a glass plate, invert it, and stand it upon a covered bottle of ammonia gas. Remove both plates at once, and hold the bottles together by grasping them firmly about their necks. Describe the action, giving all the evidence of chemical action. What is the white product?

#### Experiment 47.—Properties of Ammonium Hydroxide.

Remove the bottle in which the ammonia gas is being absorbed (see Exp. 45, (b)), and study the resulting ammonium hydroxide as follows:—

(a) Determine the general properties, *e.g.* taste and odor (cautiously), feeling, action with litmus.

(b) Warm a little in a test tube. What gas is evolved?

(c) Add ammonium hydroxide to a solution of alum. The precipitate is aluminium hydroxide. Describe it. This is a test for an hydroxide.

**Experiment 48.—Neutralization of Ammonia.** *Materials:* Ammonium hydroxide, hydrochloric acid, evaporating dish, sodium hydroxide solution, litmus paper, gauze-covered ring.

## Experiments.

Fill an evaporating dish one fourth full of ammonium hydroxide, and slowly add dilute hydrochloric acid, stirring constantly, until the solution is just neutral or faintly basic. Evaporate to dryness, very slowly, on a gauze-covered ring. Test portions of the residue thus:—

- (a) Is it an acid, alkali, or salt?
- (b) Warm a little with sodium hydroxide solution. What gas is formed? Draw a conclusion as to the nature of the original residue.
- (c) Support the dish on the gauze and warm gently until fumes are formed. What compound do the fumes suggest?
- (d) Verify the observations and conclusions by repeating (b) and (c) with ammonium chloride from the laboratory bottle.
- (e) What is the solid product of the interaction of ammonium hydroxide and hydrochloric acid?

**Experiment 49.—Preparation of Nitric Acid.** *Materials:* Glass stoppered retort, iron stand, ring, gauze, bottle, 30 grams sodium nitrate, 20 cubic centimeters concentrated sulphuric acid, funnel.

Weigh the sodium nitrate and slip it into the retort (see Int. § 6 (1) (c)). Fill the bottle nearly full of water. Put a large empty test tube into the bottle, insert the neck of the retort into the test tube, and clamp the apparatus as shown in Fig. 106 a.

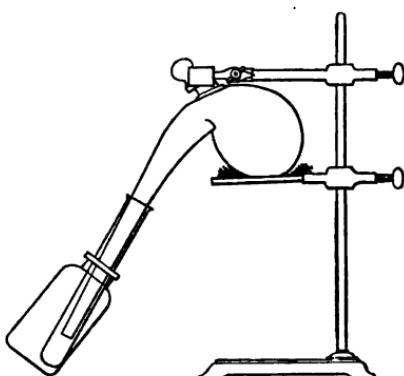


FIG. 106 a.—Apparatus for preparing nitric acid.

Stand a funnel in the tubule of the retort, and pour the acid through the funnel. Remove the funnel and insert the stopper of the retort tightly. Heat gently as long as any nitric acid runs down the neck of the retort into the test tube.

Pour the nitric acid into a test tube or small bottle for Experiment 50. Allow the

contents of the retort to cool, add a little water, boil until the contents are loosened, and then pour into a bottle for Experiment 53.

**Experiment 50.—Properties of Nitric Acid.** *Materials:* Quill toothpick, indigo solution. Add twice its volume of water to the nitric acid prepared in Experiment 49, and proceed as follows:—

(a) Warm a piece of a quill toothpick in a portion of this diluted nitric acid. How is the quill changed at first? What is the effect of continued heating? Pour off the acid, and wash the quill with water. Is the color permanent?

(b) Add a dozen or more drops of nitric acid to a *dilute* solution of indigo. Describe the change. Will ammonium hydroxide restore the original color? Is the change temporary or permanent? What, in all probability, is the general character of the change—combination or decomposition? Draw a general conclusion from (a) and (b) regarding the action of nitric acid on organic matter, which is typified by the quill and indigo.

**EXERCISES:**

- (1) What color has nitric acid?
- (2) Examine a bottle of nitric acid which has been standing in the laboratory. What can be said of the stability of nitric acid?
- (3) State other properties of nitric acid you have observed.

**Experiment 51.—Test for Nitric Acid and Nitrates.** *Materials:* Concentrated nitric and sulphuric acids, ferrous sulphate, sodium nitrate.

To a test tube one fourth full of water add a little concentrated nitric acid and shake. Add an equal volume of concentrated sulphuric acid. Shake until the acids are well mixed, then cool by holding the test tube in running water. Make a cold, dilute solution of fresh ferrous sulphate and pour this solution carefully down the side of test tube upon the nitric acid mixture. Where the two solutions meet, a brown or black layer will appear, consisting of a compound formed by the interaction of the nitric acid and the ferrous sulphate. It is an unstable compound and will often decompose if the test tube is shaken. Record the observation.

This test is also used for a nitrate. Try it with a concentrated solution of sodium nitrate in place of nitric acid. Record the result.

**Experiment 52.—A Special Test for Nitrates.** *Materials:* Charcoal, block of wood, potassium nitrate.

Heat a piece of charcoal in the Bunsen flame, lay it on a block of wood or an iron pan, and cautiously sprinkle powdered potassium ni-

## Experiments.

trate upon the hot surface. Stand back when the action begins. Observe and describe the action, especially its violence and rapidity, also the color of the flame, the effect on the charcoal, and any other characteristic result. This kind of chemical action is called *deflagration*. What causes it?

**Experiment 53.—The Solid Product of the Interaction of Sodium Nitrate and Sulphuric Acid.** *Materials:* Residue from Experiment 49, evaporating dish, glass rod, gauze-covered ring, distilled water, barium chloride solution, ferrous sulphate, concentrated sulphuric acid.

Pour a little of the solution from Experiment 49 into an evaporating dish, and evaporate to dryness over a piece of wire gauze in the hood. As the mass approaches pasty consistency, lessen the heat to avoid spattering. Continue to heat the molten mass as long as white, choking fumes are evolved. This last operation is done to remove all traces of sulphuric acid, and to complete the chemical change. Allow the dish to cool gradually, and when cool, dissolve some of the white solid in distilled water and test separate portions for a sulphate and nitrate (see Exps. 12 (c) and 51). Which is it? Test another portion for sodium by heating a little on a wire in the flame (see Exp. 24 (d)). What is the name of the white substance?

Draw a general conclusion regarding the chemical action which occurs in the preparation of nitric acid by the interaction of sulphuric acid and sodium nitrate.

**Experiment 54.—Interaction of Nitric Acid and Metals.** *Materials:* Zinc, copper, tin, iron, concentrated nitric acid.

Stand four test tubes in the test-tube rack, and slip into them a few small pieces of one of the following metals: zinc, copper, tin, and iron. Add to each test tube in succession enough concentrated nitric acid to cover the metal. Observe the changes, particularly (1) the vigor of the action, (2) the nature and properties of the products, especially color and solubility, and (3) evidence of the evolution of hydrogen. Tabulate these observations.

**Experiment 55.—Interaction of Nitric Acid and Copper, and Study of Nitric Oxide and Nitrogen Peroxide.** *Materials:* 10 grams copper (borings or fine pieces of sheet metal), concentrated nitric acid, pneumatic trough filled as usual, three bottles, three glass

plates, matches, piece of wire (15 centimeters or 6 inches long); and the *apparatus* used in Exp. 8 (modified, if desired, as in Exp. 96).

Arrange the apparatus as in Experiment 8, after putting the copper into the test tube (see Fig. 103). Adjust the delivery tube, fill three bottles with water, and invert them in the trough. Dilute 20 cubic centimeters of concentrated nitric acid with an equal volume of water, and pour just enough of this dilute acid through the safety tube into the test tube to cover the copper, taking care to seal the bend of the safety tube with acid. If the action is too vigorous, add water through the safety tube; if too weak, add acid. Collect three bottles of the gas. Cover them with glass plates and stand them aside until needed. Filter the blue liquid in the test tube into an evaporating dish, and evaporate slowly to half its volume (not to dryness) on a gauze-covered ring in the hood. The blue residue, after being dried with filter paper, should be preserved in a well-stoppered bottle.

While the solution is evaporating, study the gas as follows:—

(a) Observe its general properties while covered.

(b) Uncover a bottle. Describe the result. Is the brown gas identical in color with the one observed in the generator at the beginning of the experiment?

(c) Uncover a bottle, pour in about 25 cubic centimeters of water, cover with the hand and shake vigorously, still keeping the bottle covered. Why has the brown gas disappeared? Uncover the bottle for an instant, then cover and shake again. Is the result the same? Repeat, if the result is not definite, or does not agree with previous observations.

(d) With the third bottle determine whether the brown gas will burn or support combustion. A convenient flame is a burning match fastened to a stiff wire. Plunge it quickly to the bottom at first and gradually raise it into the brown gas.

**ANSWER :**

(1) What is the source of the colorless gas? What is its name? What is the name of the brown gas?

(2) What is the general chemical relation of the two gases to each other? To the air?

(3) Why is not the brown gas collected in the bottles by displacement of water?

(4) Will either gas burn or support combustion?

(5) Which gas has been observed before? In what experiment?  
 (6) What is the general relation of these gases to nitric acid?

Study the properties of the crystals by determining:—

- (a) Solubility in water (cold and hot).
- (b) Effect of intense heat.
- (c) Action of their solution upon an iron nail.
- (d) Action of their solution when added to ammonium hydroxide.
- (e) Presence of a nitrate.

Compare the observed properties with those of copper nitrate obtained from the laboratory bottle. Are the two substances identical?

**Experiment 56.—Preparation and Properties of Nitrous Oxide.**

*Materials:* Ammonium nitrate, pneumatic trough, wad of iron thread, copper wire, three bottles, three glass plates, sulphur, deflagrating spoon, a joss stick. The apparatus is shown in Figure 107. The parts lettered *A*, *C*, *D*, *E* have been used before; *B*, *F*, *G*, *H* are exactly the same as *A*, *C*, *D*, *E* respectively. (See page 504.)

Construct and arrange the apparatus as shown in the figure. Fill the large test tube, *A*, about half full of ammonium nitrate. The large test tube, *B*, remains empty. The end of *H* rests on the bottom of the pneumatic trough as usual. It is desirable, though not absolutely necessary, to fill the trough and bottles with *warm* water. Be sure the apparatus is gas-tight.

Heat *A* gently with a low flame (5 centimeters or 2 inches). Adjust the apparatus if it leaks. The ammonium nitrate melts and appears to boil. Regulate the heat so that the evolution of the nitrous oxide will be slow. Notice the fumes which collect in *A*, and the liquid which collects in *B*. Prepare three bottles of nitrous oxide, free from air, covering each with a glass plate as soon as removed from the trough. When the last bottle has been collected and covered, remove the end of the delivery tube from the trough.

Test the gas as follows:—

(a) Allow a bottle to remain uncovered for a few seconds. How does nitrous oxide differ from nitric oxide?

(b) Thrust a glowing joss stick into the same bottle of gas. Describe the result. Is the gas combustible? Does it support combustion?

(c) The observations in (b) suggest that the gas is oxygen, but it is not, though this fact is not easily proved by a single experiment. Put

a small piece of sulphur in a deflagrating spoon, light it, and lower the burning sulphur *at once* into another bottle of gas. If the experiment is conducted properly, the sulphur will not burn so brightly as it would in a bottle of oxygen.

(d) Twist one end of the copper wire around a wad of iron thread. Heat the edge of the wad an instant in the flame and then lower it quickly into a bottle of the gas. Observe the change. Recall a similar experiment with oxygen. Compare the two results.

What in all probability is the other product (seen in *B*) of the chemical change in this experiment? Could it have been an impurity in the ammonium nitrate? What are the fumes noticed in *A*?

How would you distinguish ammonium nitrate from all other nitrates? How would you distinguish nitrous oxide from (a) the other oxides of nitrogen, (b) air, (c) oxygen, (d) hydrogen, (e) nitrogen, (f) carbon dioxide?

**Experiment 57.—Preparation and Properties of Sodium Nitrite.**  
*Materials:* 10 grams sodium nitrate, 20 grams lead, iron pan, glass rod.

Heat the mixture of lead and sodium nitrate on the iron pan, which is supported on the ring of an iron stand. Stir the melted mass with a glass rod. Some of the lead will disappear and a yellowish brown powder will be seen in the molten mass. The action should proceed until most of the lead has disappeared. Allow the mass to cool, cover it with water, heat the water to boiling in the pan, let it cool and then filter; add water to the residue, boil, and filter this portion. This operation extracts the sodium nitrite. Add to the combined filtrates several drops of concentrated sulphuric acid. Describe the result. How does the result compare with the action of concentrated sulphuric acid on sodium nitrate? The yellowish product is lead oxide. What general chemical change led to its formation? How must the nitrate have been changed?

**Experiment 58.—Aqua Regia.** *Materials:* Gold leaf, concentrated nitric and hydrochloric acids, glass rod.

Touch a small piece of gold leaf with the end of a moist glass rod, and wash the gold leaf into a test tube by pouring a few cubic centimeters of concentrated hydrochloric acid down the rod. Heat gently until the acid just begins to boil. Does the gold dissolve? Wash an-

## Experiments.

other piece of gold leaf into another test tube with concentrated nitric acid, and heat as before. Does the gold dissolve? Pour the contents of one tube into the other, and warm gently. Does the gold dissolve? Draw a conclusion regarding the solubility of gold.

**ANSWER :**

- (1) What is the literal meaning and significance of the term *aqua regia*?
- (2) What other metals does *aqua regia* dissolve?
- (3) What is the chemical action of *aqua regia* on gold?
- (4) Upon what property of nitric acid does the action of *aqua regia* depend?

**CARBON.**

**Experiment 59.—Distribution of Carbon.** *Materials:* Hessian crucible, sand, wood, cotton, starch, sugar, glass tube (or rod), candle, block of wood.

(a) Cover the bottom of a Hessian crucible with a thin layer of sand. Put on the sand a small piece of wood, a small, compact wad of cotton, and a lump of starch. Fill the crucible loosely with dry sand, and slip it into the ring of an iron stand. Heat with a flame which extends just above the bottom of the crucible until the smoking ceases (approximately 20 minutes). After the crucible has cooled sufficiently to handle, pour the contents out upon a block of wood or an iron pan. Examine the contents. What is the residue? What is hereby shown about the distribution of carbon?

While the crucible is heating, do the following: —

(b) Heat about 1 gram of sugar in an old test tube until the vapors cease to appear. What is the most obvious product?

(c) Close the holes at the bottom of a lighted Bunsen burner, and hold a glass tube in the upper part of the flame long enough for a thin deposit to form. Examine it, name it, and state its source.

(d) Hold a glass tube in the flame of a candle which stands on a block of wood, and compare the result with that in (c).

Draw a general conclusion regarding the distribution of carbon.

**Experiment 60.—Decolorizing Action of Charcoal.** *Materials:* Animal charcoal, indigo solution, filter paper and funnel.

Fill a test tube one fourth full of powdered animal charcoal as follows: Fold a narrow strip of smooth paper so that it will slip easily into the

test tube; place the powder at one end of the troughlike holder, slowly push the paper into the test tube, holding both tube and paper in a horizontal position; now hold the tube upright, and the powder will slip from the paper. Add 10 cubic centimeters of indigo solution, shake thoroughly for a minute, and then warm gently. Filter through a wet filter paper into a clean test tube. Compare the color of the filtrate with that of the indigo solution. Explain the change in color.

Other organic substances besides indigo are similarly changed. Draw a general conclusion regarding the decolorizing power of charcoal.

**Experiment 61. — Deodorizing Action of Charcoal.** *Materials:* Wood charcoal, hydrogen sulphide solution, test tube, and cork.

Smell of a weak solution of hydrogen sulphide gas. Fill a test tube half full of powdered wood charcoal as in Experiment 60, add a little hydrogen sulphide solution, and cork securely. If the tube leaks, make the opening gas-tight with vaseline. Shake thoroughly. After fifteen or twenty minutes, remove the stopper and smell of the contents. Is the odor much less offensive? Repeat, unless a definite result is obtained. Explain the change.

**Experiment 62. — Preparation of Carbon Dioxide.** *Materials:* Lumps of marble, sand, concentrated hydrochloric acid, stick of wood, candle fastened to a wire, limewater, four bottles. Use the same *apparatus* as in the preparation of hydrogen (see Exp. 8).

Cover the bottom of the test tube with sand, add a little water, and carefully slip into it half a dozen small lumps of marble. Arrange the apparatus to collect the gas over water, as previously directed. Add through the safety tube just enough concentrated hydrochloric acid to cover half the marble. Collect four bottles, cover with glass plates or filter paper, and stand aside till needed.

Allow the action in the tube to continue, and preserve the contents for Experiment 64.

Proceed at once to the next experiment.

**Experiment 63. — Properties of Carbon Dioxide.**

Study the properties of carbon dioxide gas as follows:—

(a) Plunge a blazing joss stick several times into a bottle. Describe the result.

(b) Lower a lighted candle into a bottle of air, and invert a bottle of carbon dioxide over it, holding the bottles mouth to mouth. Describe the result. What does this result show about the density of carbon dioxide?

(c) Pour a little limewater into a bottle of carbon dioxide, cover with the hand, and shake vigorously. Describe and explain the result.

(d) Fill a bottle of carbon dioxide one third full of water, cover tightly with the hand, and shake vigorously. Invert, still covered, in the pneumatic trough. Does the result reveal any facts about the solubility of carbon dioxide?

#### EXERCISES :

(1) Describe the preparation of carbon dioxide.

(2) What do (a) and (b) show about the relation of carbon dioxide to combustion?

(3) What is the test for carbon dioxide?

(4) What chemical changes occur in the test for carbon dioxide?

#### **Experiment 64.—The Solid Product of the Interaction of Calcium Carbonate and Hydrochloric Acid.**

Filter the contents of the test tube (from Exp. 62) into an evaporating dish, adding a little warm water beforehand, if the contents is solid. Stand the dish on a gauze-covered support and evaporate to dryness in the hood. As the residue approaches pasty consistency heat gently to avoid spattering, and finally add enough water to dissolve the whole mass; evaporate again to dryness. Heat the residue until no fumes of hydrochloric acid are evolved. Dissolve some of the residue in distilled water and test portions for (a) a chloride and (b) a calcium compound (see Exp. 12 (b), (d)). If a calcium compound is found, confirm the observation thus: Dip a clean, moist platinum test wire (see Int. § 5 (4)) into the solid residue, and hold it in the Bunsen flame. If calcium is present, the flame will be colored a yellowish red.

What is the residue? Verify the conclusion by a simple experiment.

#### **Experiment 65.—Carbon Dioxide and Combustion. Materials:** Limewater, glass tube, candle attached to wire, stick of wood, two bottles.

(a) Exhale through a glass tube into a test tube half full of lime-water. Describe and explain the result.

(b) Lower a lighted candle into a bottle and allow it to burn for a few minutes. Remove the candle, pour a little limewater into the bottle, and shake vigorously. Describe and explain the result.

(c) Allow a stick of wood to burn for a short time in a bottle (not the one used in (b)), and then proceed as in (b). Describe the result. Does it confirm the results obtained in (a) and (b)?

(d) Repeat (c), using a piece of paper in place of the wood. Describe the result. Does it confirm the results obtained in (a), (b), and (c)?

**ANSWER:**

(1) What is the source of the carbon dioxide in (a)?

(2) What is one of the gases escaping from chimneys? From a burning lamp?

**Experiment 66.—Carbonic Acid. (Teacher's Experiment.)**

**Materials:** Solutions of sodium hydroxide and phenolphthalein, bottle, and the carbon dioxide generator used in Experiment 62.

Construct and arrange the carbon dioxide generator as in Experiment 62. Fill a bottle nearly full of water, add a few drops of a solution of phenolphthalein<sup>1</sup> and just enough sodium hydroxide solution to color the liquid a faint magenta. Allow a *slow* current of carbon dioxide to bubble through the liquid in the bottle, until a definite change is produced in the absorbing liquid. Describe and explain it.

**Experiment 67.—Preparation and Properties of Carbonates.**

**Materials:** Marble, sand, concentrated hydrochloric acid, limewater. The *apparatus* is the same as that used in Experiment 62.

(a) Prepare a carbon dioxide generator as in Exp. 62, and attach it by a clamp to an iron stand so that the end of the delivery tube reaches to the bottom of a bottle half full of limewater. Pass the gas *slowly* into the limewater until considerable precipitate is formed. Remove the bottle and let the precipitate settle.

(b) Meanwhile pass carbon dioxide *slowly* for about ten minutes into a bottle half full of a solution of sodium hydroxide.

(c) Examine the precipitate from (a) as follows: Pour off most of the liquid without disturbing the solid (see Int. § 6 (1) (a)). Dip a glass tube into limewater, remove it, and a drop will adhere to the end.

<sup>1</sup> This compound is magenta in alkaline solutions and colorless in acid solutions.

## Experiments.

Pour a little dilute hydrochloric acid into the bottle, shake, and hold the "limewater tube" in the escaping gas. Observe the change in the drop of limewater. If no change occurs, add more acid to the precipitate. What is the liberated gas? What is the precipitate? How was the latter formed?

(d) Proceed as in (c) with the solution obtained in (b). What is the liberated gas? From what compound did it come? How was this compound formed? How does it differ from the one formed in (a)?

**ANSWER :**

- (1) What is the test for a carbonate?
- (2) How may limewater be distinguished from a solution of sodium or potassium hydroxide?

**Experiment 68.—Detection of Carbonates.** *Materials:* Hydrochloric acid, limewater, glass tube; baking soda, washing soda, baking powder, native chalk, tooth powder, white lead, whiting, old mortar (or plaster).

Put a little of each of the above solids in separate test tubes, add a little water and dilute hydrochloric acid, and shake; hold the "limewater tube" in the escaping gas, as in Experiment 67. If the action is not marked, warm the test tube. Describe the result in each case.

**Experiment 69.—Acid Calcium Carbonate.** *Materials:* Limewater and the carbon dioxide generator used in Experiment 62.

Pass carbon dioxide into a test tube half full of limewater until the precipitate disappears. Filter, if the liquid is not perfectly clear, and then heat. Describe the change. Explain the three changes which take place in the test tube.

**Experiment 70.—Preparation and Properties of Carbon Monoxide. (Teacher's Experiment.)** *Materials:* Oxalic acid, concentrated sulphuric acid, limewater, pneumatic trough filled as usual, three bottles, three glass plates. The *apparatus* is shown in Figure 107 (p. 504).

**Precaution.** *Carbon monoxide and oxalic acid are poisonous. Hot sulphuric acid is dangerous. Perform this experiment with unusual care.*

Put 10 grams of oxalic acid in the large test tube, *A*, and add 25 cubic centimeters of concentrated sulphuric acid. Put enough lime-water in *B* to cover the end of the tube, *E*. The end of *H* should rest

on the bottom of the pneumatic trough just beneath the hole in the shelf. Heat the tube, *A*, gently, and carbon monoxide will be evolved. A small flame must be used, because the gas is rapidly evolved as the heat increases. It is advisable to remove or lower the flame as bubbles appear in the tube, *B*, — *regulate the heat by the effervescence*. Collect all the gas, but do not use the first bottle, covering the bottles with glass plates as they are filled, and setting them aside temporarily. When the last bottle has been collected and covered, loosen the stopper in *B*, remove the end of *H* from the water in the trough, and if gas is still being evolved, stand the whole apparatus in the hood.

Test the gas thus: —

- (a) Notice that it is colorless.
- (b) Hold a lighted match at the mouth of a bottle for an instant. Note the flame, especially its color and how it burns. After the flame has disappeared, drop a lighted match into the bottle. Describe the result. Draw a conclusion and verify it by (c).
- (c) Burn another bottle of gas, and after the flame has disappeared pour limewater into the bottle and shake. Describe the result.

#### EXERCISES FOR THE CLASS:

- (1) What gas besides carbon monoxide was produced, as shown by *B*?
- (2) Summarize the observed properties of carbon monoxide.
- (3) What is the chemical relation of the two oxides of carbon?
- (4) How can the two oxides be changed into each other? What two general processes do the changes illustrate?

**Experiment 71.—Preparation and Properties of Ethylene.**  
**(Teacher's Experiment.) Materials:** Alcohol, concentrated sulphuric acid, sand, pneumatic trough filled as usual, two bottles, limewater. The *apparatus* is that used in Experiment 70.

**Precaution.** *A mixture of ethylene and air explodes, if ignited. Hot sulphuric acid is dangerous. Guard against flames, leaks, and breakage.*

Put 5 cubic centimeters of water in a test tube and slowly pour upon it 15 cubic centimeters of concentrated sulphuric acid. Cool the acid by holding the test tube in a stream of cold water. Put 5 to 7 cubic centimeters of alcohol in the test tube, *A*, add a little clean sand, and

## Experiments.

then slowly pour in the *cold* acid. The test tube, *B*, remains empty. A dish should stand under *A* to catch the contents, in case of accident.

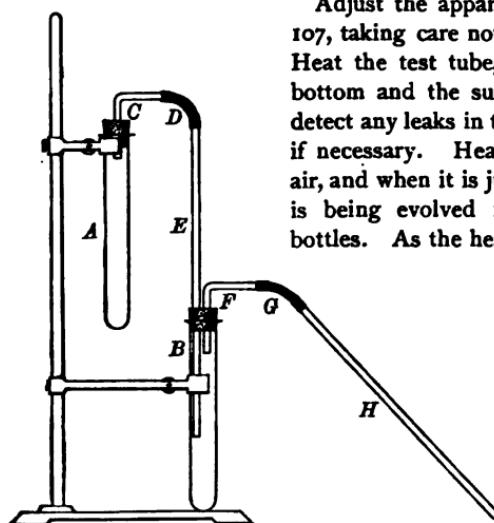


FIG. 107.—Apparatus for preparing ethylene.

Adjust the apparatus as shown in Figure 107, taking care not to crush the test tubes. Heat the test tube, *A*, gently between the bottom and the surface of the contents to detect any leaks in the apparatus. Readjust, if necessary. Heat gently to drive out the air, and when it is judged that the gas which is being evolved is ethylene, collect two bottles. As the heat increases, the mixture is apt to froth or "bump"; sometimes the gas is evolved suddenly. Hence the heat must be so regulated that the evolution of gas is slow. Especial care must be taken not to heat the test tube above the surface of the contents, otherwise

a sudden movement of the hot liquid might crack the test tube. As soon as the gas has been collected, remove the tube, *H*, from the water, and if the ethylene is still being evolved, stand the apparatus in the hood. When the tube, *A*, is cool enough to handle, pour the contents down the sink or into a receptacle especially provided for dangerous mixtures.

Test the gas by holding a lighted match at the mouth of a bottle. Observe and record the color and temperature of the flame, its luminosity, rapidity of combustion, visible products, and any other characteristic properties. Repeat with the other bottle, and carefully observe properties needing confirmation. Add a little limewater to one of the bottles in which the gas was burned, shake, and explain the result. What evidence does this experiment present regarding the composition of ethylene?

### **Experiment 72.—Preparation and Properties of Acetylene.**

Fill a test tube nearly full of water, stand the test tube in a rack, and drop two or three very small pieces of calcium carbide into the test

tube. Acetylene is evolved. After the action has proceeded long enough to expel the air, light the gas by holding a lighted match at the mouth of the tube. Observe and record the nature of the flame.

Attach an acetylene burner by a short rubber tube to a short glass tube inserted in a one-hole rubber stopper. Put 10 cubic centimeters of water in a test tube, drop in a very small lump of calcium carbide, insert the stopper, and light the gas cautiously. Describe the flame.

**Experiment 73.—Preparation and Properties of Illuminating (Coal) Gas. (Teacher's Experiment.)** *Materials:* Soft coal, asbestos, pneumatic trough filled as usual, three bottles, litmus paper, filter paper, lead acetate (or nitrate) solution. The apparatus is shown in Figure 108. *AA'* is an ignition tube from 10 to 15 centimeters (4 to 6 inches) long. A spiral of copper wire is placed near *A'*, and the tube is supported by a

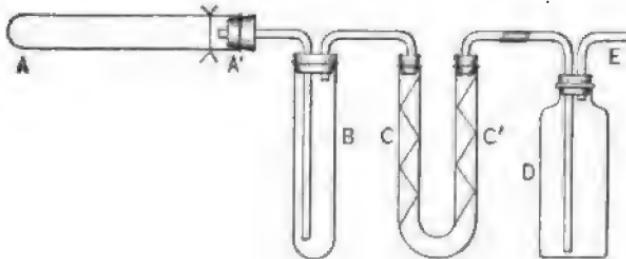


FIG. 108.—Apparatus for preparing illuminating gas from soft coal.

clamp between the wire and the end of the tube. An empty test tube or bottle is connected with the combustion tube by a bent tube passing to the bottom of *B*; this vessel retains tarry matter, which comes from the ignition tube. The U-tube contains moistened pink litmus paper in the limb *C*, and a narrow strip of filter paper moistened with a lead compound (nitrate or acetate) in the limb *C'*, the latter serving to detect hydrogen sulphide. The bottle, *D*, which may be any convenient size, is connected as shown in the figure, and is to be one third full of lime-water. The tube, *E*, is to be connected with a delivery tube passing into a pneumatic trough arranged to collect a gas over water.

Fill *AA'* two thirds full of coarsely powdered soft coal, which should be held in place with a loose plug of shredded asbestos. See that all connections are gas-tight by heating the ignition tube gently; if the apparatus is tight, the expanded air will bubble through the bottle *D*. Readjust, if necessary.

Heat the whole ignition tube gently at first, and gradually increase the heat, but avoid heating either end very hot, otherwise the closed end may soften and burst or the rubber stopper may melt. As the heat increases, watch for marked changes in *B*, *CC'*, and *D*. As soon as the slow bubbling shows that all air has been driven out of the apparatus, collect, as previously directed, two bottles of the gas evolved. Cover the bottles with wet filter paper as soon as they are removed from the trough. When the last bottle has been removed, disconnect the apparatus at any convenient point between *A'* and *C*. Let the ignition tube cool.

Test the gas by holding a lighted match near the mouth of a bottle. Observe and record the color and heat of the flame. Is smoke formed? Repeat with the remaining bottle, and observe more closely any facts suggested, but not clearly shown, by the first observations.

Examine the contents of the ignition tube. Does it resemble coke or some form of carbon? Examine the bottle, *B*, for tarry matter. Does the paper in *C* show the formation of ammonia? If the paper in *C* is black or brown, it is caused by lead sulphide, which is formed by the interaction of hydrogen sulphide and a lead compound. Did the gas contain hydrogen sulphide? Did the bottle, *D*, show the formation of carbon dioxide?

#### EXERCISES FOR THE CLASS:

- (1) Describe briefly the whole experiment.
- (2) Sketch the apparatus.
- (3) Summarize the properties of coal gas.

#### Experiment 74.—Combustion of Illuminating Gas. *Materials:* Pointed glass tube (see Int. § 3 (c)), bottle, limewater.

Remove the Bunsen burner from the rubber connection tube and replace it by a glass tube with a small opening. Light the gas, and lower a small flame into a cold, dry bottle. Observe at once the most definite result inside the bottle. Remove and extinguish the flame, add a little limewater to the bottle, and shake. What are the two products of the combustion of coal gas?

#### Experiment 75.—Construction of a Bunsen Burner.

Take apart a Bunsen burner and study the construction. Write a short description of the burner. Sketch the essential parts.

**Experiment 76.—Bunsen Burner Flame.** *Materials:* Glass tube, powdered wood charcoal, pin, copper wire, wire gauze.

I. (a) Close the holes at the bottom of a Bunsen burner and hold a glass tube in the upper part of the flame. Note the black deposit. What is it? Where did it come from? Open the holes and hold the blackened tube in the colorless flame. What becomes of the deposit? How is the flame changed, if at all? What does the experiment suggest about the luminosity of flame?

(b) Dip a glass tube a short distance into powdered wood charcoal, place the end containing the charcoal in one of the holes at the bottom of the burner, and blow gently two or three times into the other end. Describe and explain the result. Does it verify the answer to the last question in (a)?

(c) Open and close the holes of a lighted burner several times. Describe the result. Pinch the rubber tube to extinguish the flame, then light the gas at the holes. What change is produced in the flame? What causes the change?

**ANSWER :**

- (1) What is the object of the holes?
- (2) Why does the gas burn at the top and not inside of the burner?
- (3) Why does the flame sometimes "strike back" and burn inside?
- (4) Why is the Bunsen flame nonluminous?

II. (a) Hold a match across the top of the tube of a lighted Bunsen burner. When it begins to burn, remove and extinguish it. Note where it is charred, and explain the result.

Press a piece of wire gauze down upon the flame. Describe the appearance of the gauze.

The same fact may be

shown by sticking a pin through a (sulphur) match, suspending it across the burner, and then lighting the gas. The position of the match is shown in Figure

109. Turn on a full current of gas before lighting it. What does the whole

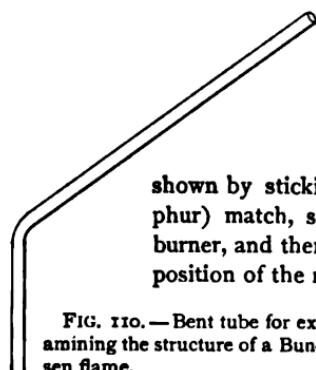


FIG. 110.—Bent tube for examining the structure of a Bunsen flame.

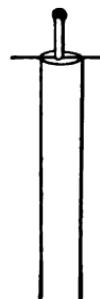


FIG. 109.—Sulphur match suspended across the top of a Bunsen burner.

experiment show about the structure of the lower part of the Bunsen flame? Verify your answer by (b).

(b) Bend a glass tube about 15 centimeters (6 inches) long into the shape shown in Figure 110. Hold the shorter arm in the flame about 2 centimeters (1 inch) from the top of the burner tube. Hold a lighted match for an instant at the upper end of the tube. What does the result show about the structure of the Bunsen flame? Does it verify (a)?

(c) Find the hottest part of the flame, when a full current of gas is burning, by holding a copper wire in the flame. Measure its distance, approximately, from the top of the burner tube.

(d) Examine a typical Bunsen flame — one which shows clearly the outlines of the inner part. What is the general shape of each main part? Draw a vertical and a cross section of the flame.

**Experiment 77.—Candle Flame.** *Materials:* Candle, two blocks of wood, bottle, piece of stiff white paper, limewater, matches, lamp chimney, copper wire (15 centimeters or 6 inches long).

Attach a candle to a block of wood by means of a little melted candle wax, and proceed as follows:—

(a) Hold a cold, dry bottle over the lighted candle. Describe the result produced inside the bottle. What is the product? What is its source? Remove the bottle, pour a little limewater into it, and shake. Describe and explain the result. What are the two main products of a burning candle?

(b) Blow out the candle flame, and immediately hold a lighted match in the escaping smoke. Does the candle relight? Why? What is the general nature of this smoke? How is it related to the candle wax? How do (b) contribute to the explanation of (a)?

(c) Press a piece of stiff white paper for an instant down upon the candle flame almost to the wick. Repeat several times with different parts of the paper. What does the paper show about the structure of the flame?

(d) Stand a lamp chimney over the lighted candle. How is the flame affected? Hold the chimney a short distance (1 centimeter or .5 inch) above the block. Does the candle continue to burn? Why? Keep the chimney in the same position and cover the top with a block of wood. What is the result? Why?

(e) Roll one end of the copper wire around a lead pencil to form a spiral about (2 centimeters or 1 inch) long. Press the spiral down upon the candle flame. What is the result? Why?

**EXERCISES:**

- (1) Draw a candle flame, showing the parts.
- (2) What is the essential difference between a candle flame and a Bunsen flame?
- (3) Is there any essential difference between a candle flame and a gas or a lamp flame?
- (4) Why do candles and lamps often smoke?

**Experiment 78. — Kindling Temperature.**

(a) Press a wire gauze down upon a Bunsen flame. Where is the flame? Let the gauze cool, lower it upon the flame, and hold a lighted match just above the gauze. Now where is the flame?

(b) Extinguish the flame. Turn on the gas, hold the gauze in the escaping gas, about 15 centimeters (6 inches) above the top of the burner, and thrust a lighted match into the gas above the gauze. Where is the flame? Lower the gauze slowly and describe the final result.

(c) Hold the gauze in the flame in one position for a minute or two. Where is the flame at the end of this time? Why?

**EXERCISES:**

- (1) Define kindling temperature.
- (2) What application is made of the principle illustrated by this experiment?
- (3) State exactly how this experiment illustrates kindling temperature.

**Experiment 79. — Reduction and Oxidation with the Blowpipe.** *Materials:* Blowpipe, blowpipe tube, charcoal, lead oxide (litharge), sodium carbonate, sodium sulphate, wood charcoal, silver coin, zinc, lead, tin.

Slip the blowpipe tube into the burner, light the gas and lower the flame until it is about 4 centimeters (1.5 inches) high. Rest the tip of the blowpipe on the top of the tube, placing the tip just within the flame. Put the other end of the blowpipe between the lips, puff out the cheeks, inhale through the nose, and exhale into the tube, using the cheeks somewhat as a bellows. Do not blow in puffs, but produce a continuous flow of air by steady and easy inhaling and exhaling. The operation is nat-

## Experiments.

ural and simple, and, if properly performed, will not make one out of breath. The flame should be an inner blue cone surrounded by an outer and almost invisible cone, though its shape varies with the method of production (see Fig. 44). Practice until the flame is produced voluntarily and without exhaustion. Watch the flame and learn to distinguish the two parts, so that they may be intelligently utilized.

I. *Reduction.* (a) Make a shallow hole at one end of the flat side of a piece of charcoal. Fill the hole with a mixture of equal parts of powdered sodium carbonate and lead oxide, and heat the mixture in the reducing flame. The sodium carbonate melts and assists the fusion of the oxide, but the former is not changed chemically. In a short time bright, silvery globules will appear on the charcoal. Let the mass cool, and pick out the largest globules. Put one or two in a mortar, and strike with a pestle. Are they soft and malleable, or brittle and hard? State the result when a globule is drawn across or rubbed upon a white paper. How do the properties compare with those of metallic lead? What has become of the oxygen? Of what chemical use is the charcoal?

(b) Grind together in a mortar a little sodium sulphate and wood charcoal, adding at intervals just enough water to hold the mass together. Heat this paste for a few minutes in the reducing flame as in (a). Scrape the fused mass into a test tube, boil in a little water, and put a drop of the solution on a bright silver coin. If a dark brown stain is produced, it is evidence of the formation of silver sulphide. Repeat, if no such stain is produced. State all the chemical changes which led to the production of the silver sulphide, explaining at the same time how the experiment illustrates reduction.

II. *Oxidation.* (a) Heat a small piece of zinc on charcoal in the oxidizing flame. What is the product? Observe its color, and the color of the coating on the charcoal when hot and cold. Record as described in (d).

(b) Heat a piece of lead as in (a). Observe the presence or absence of fumes, as well as the color of the coating when hot and cold. See (d).

(c) Heat a small piece of tin in the oxidizing flame. Observe as in (b).

(d) Tabulate the above observations, stating (1) the color of the hot and cold coating on the charcoal, (2) presence or absence of fumes, (3) name of product.

### EXERCISES:

(1) Sketch a blowpipe.

(2) Sketch a flame showing the oxidizing and reducing parts.

## FLUORINE, BROMINE, AND IODINE.

**Experiment 80.—Preparation and Properties of Hydrofluoric Acid.** *Materials:* Lead dish, glass plate, paraffin, file, calcium fluoride, concentrated sulphuric acid.

**Precaution.** *Hydrofluoric acid gas is a corrosive poison. An aqueous solution of the gas—commercial hydrofluoric acid—burns the flesh frightfully.*

Warm a glass plate about 10 centimeters (4 inches) square by dipping it into hot water or by standing it near a warm object, such as a radiator. If it is held over a flame, it is liable to crack. Coat one surface with paraffin. The surface should be uniformly covered with a thin layer. Scratch letters, figures, or a diagram through the wax with a file. Be sure the instrument removes the wax through to the glass, and that the lines are not too fine.

Put 5 grams of calcium fluoride in a lead dish and add just enough concentrated sulphuric acid to form a thin paste. Stir the mixture with a file. Place the glass plate, wax side down, upon the lead dish and stand the whole apparatus in the hood for several hours, or until some convenient time. Remove the plate. Scrape the contents of the dish, immediately, into a waste jar in the hood, and wash the dish free from acid. Most of the wax can be scraped from the glass plate with a knife. The last portions can be removed by rubbing with a cloth moistened with alcohol or turpentine. Do not attempt to melt off the wax over the flame. If the experiment has been properly performed, the plate will be etched where the glass was exposed to the hydrofluoric acid gas.

**Experiment 81.—Preparation and Properties of Bromine.** *Materials:* Potassium bromide, manganese dioxide, dilute sulphuric acid, bottle of water, test-tube holder. The *apparatus* is shown in Figure III. The large test tube is provided with a one-hole rubber stopper to which is fitted the bent glass tube. The latter is about 30 centimeters (12 inches) long, and is bent according to the directions given in the Introduction, § 3 (b).

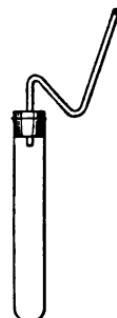


FIG. III.—Apparatus for preparing bromine.

## Experiments.

**Precaution.** *Bromine is a corrosive liquid which forms, at the ordinary temperature, a suffocating vapor. Perform in the hood all experiments which use or evolve bromine.*

Put a dozen crystals of potassium bromide in the test tube, add an equal quantity of manganese dioxide and 10 cubic centimeters of dilute sulphuric acid. Insert the stopper and its tube securely, and boil gently. Do not hold the test tube in the hand, but use the test tube holder. Brown fumes soon appear in the test tube and pass out of the delivery tube. Regulate the heating so that this vapor will condense and collect in the lower bend of the delivery tube. Both vapor and liquid are bromine. When no further boiling produces bromine vapor in the test tube, pour the bromine from the delivery tube into a bottle of water. Observe and record the physical properties of this bromine, especially the color, solubility in water, specific gravity, volatility, and physical state. Try the action of the contents of the bottle on litmus paper; if the action is not marked, push the paper down near the bromine. Determine the odor by smelling *cautiously* of the water in the bottle. As soon as these observations have been made, pour the contents of the bottle into the sink and flush with water, or pour into a jar in the hood. Wash the test tube free from all traces of bromine, taking care to get none on the hands.

**ANSWER :**

- (1) In what ways does bromine physically resemble chlorine? In what ways does it differ from chlorine?
- (2) How is it essentially different from all other elements previously studied?

**Experiment 82.—Properties of Potassium Bromide.** *Materials:* Potassium bromide, silver nitrate solution, ammonium hydroxide.

Examine a crystal of potassium bromide, and state its most obvious properties. Dissolve it in a test tube half full of water, and add a few drops of silver nitrate solution. Describe the result. Is the solid product soluble in ammonium hydroxide? How can bromides be distinguished from chlorides? Do the properties of bromides, typified by potassium bromide, suggest any marked relation to chlorides?

**Experiment 83.—Preparation and Properties of Iodine.** *Materials:* Potassium iodide, manganese dioxide, mortar and pestle, concentrated sulphuric acid, funnel, cotton.

Grind together in a mortar a dozen large crystals of potassium iodide and about twice the bulk of manganese dioxide. Put the mixture in a test tube provided with a holder, moisten with water, and add a few cubic centimeters of concentrated sulphuric acid. Plug with cotton the inside opening of a funnel, and hold the latter firmly over the mouth of the test tube. Heat the test tube gently with a low flame (5 centimeters or 2 inches). The vapor of iodine will fill the test tube, and crystals will collect in the upper part of the test tube and in the funnel. If the crystals collect in the test tube, a gentle heat will force them into the funnel. Continue to heat until enough iodine collects in the funnel for several experiments. Scrape the crystals into a dish.

Study the properties as follows: —

(a) Observe and record the physical properties of iodine, especially the color of the solid and of the vapor, volatility, and odor (cautiously).

(b) Heat a crystal in a dry test tube, and when the tube is half full of vapor, invert it. What does the result show about the density of iodine vapor?

(c) Touch a crystal with the finger. What color is the stain? Will water remove it? Will alcohol? Will a solution of potassium iodide? What do these results show about the solubility of iodine?

(NOTE. — If crystals are left, use them in the next experiment. Preserve in a stoppered bottle.)

**Experiment 84. — Test for Iodine with Carbon Disulphide.**  
Materials: Iodine, potassium iodide, carbon disulphide, chlorine water.

**Precaution.** *Carbon disulphide is inflammable. It should not be used near flames.*

(a) *Free iodine.* Add a few drops of carbon disulphide to a very dilute solution of iodine, made by dissolving a crystal of iodine in a solution of potassium iodide, and observe the color of the carbon disulphide, which, being much heavier than water, will sink to the bottom of the test tube. How does it resemble the color of iodine vapor?

(b) *Combined iodine.* Add a few drops of carbon disulphide to a very dilute solution of potassium iodide. Is there positive evidence of iodine? Now add several drops of chlorine water, and shake. How does this result compare with the final result in (a)? The result is due to the fact that chlorine liberates iodine from its compounds, and the iodine, being free, exhibits the characteristic color.

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**Experiment 85.—Test for Iodine with Starch.** *Materials:* Starch, mortar and pestle, iodine solution, potassium iodide, chlorine water.

Grind a lump of starch in a mortar with a little water to creamy consistency. Pour this into about 100 cubic centimeters of boiling water, and stir the hot liquid. Allow it to cool, or cool it by holding the vessel in a stream of cold water, and then pour off the clear liquid. Use this cold starch solution to test for iodine.

(a) *Free iodine.* Add a few cubic centimeters of the starch solution to a test tube nearly full of water, and then add a few drops of iodine solution. The deep blue color is due to the presence of a compound which is always formed under these circumstances, but the composition of which is unknown. If the color is black, pour out half of the liquid and add more water, or pour some of the liquid into a dish of water.

(b) *Combined iodine.* Add a few cubic centimeters of the starch solution to a very dilute solution of potassium iodide. Is the blue compound formed? Add a few drops of chlorine water, and shake. Compare with the final result in Experiment 84 (b).

**Experiment 86.—Detection of Starch by Iodine.** *Materials:* Dilute solution of iodine (in potassium iodide), mortar and pestle, potato, rice, bread.

Test the potato, rice, and bread for starch by grinding a little of each with water in a mortar, and then adding a few drops of the extract to a very dilute solution of iodine. State the result in each case.

**Experiment 87.—Properties of Potassium Iodide.** *Materials:* Potassium iodide, silver nitrate solution, ammonium hydroxide.

Proceed with the potassium iodide as in Experiment 82.

How can iodides be distinguished from chlorides? Do iodides, typified by potassium iodide, suggest any marked relation to bromides and chlorides?

### SULPHUR AND ITS COMPOUNDS.

**Experiment 88.—Properties of Sulphur.**

(a) Examine a lump of sulphur, and state briefly its most obvious physical properties.

(b) *Optional.* Weigh a lump of roll sulphur to a decigram. Slip it carefully into a graduated cylinder previously filled with water to a

known point — about half full — and note the increase in the volume of water. This increase in volume is equal to the volume of the sulphur. Calculate the specific gravity of sulphur from the observed data.

(NOTE.— Specific gravity equals weight in air divided by weight of equal volume of water.)

**Experiment 89.—Amorphous Sulphur.** *Materials:* Sulphur, old test tube, evaporating dish.

Put a few pieces of roll sulphur in an old test tube. Heat carefully until the sulphur boils, and then quickly pour the contents of the test tube into a dish of cold water. This is amorphous sulphur. Note its properties. Preserve, and examine it after twenty-four hours. Describe the change, if any.

Define amorphous, and illustrate it by this experiment.

**Experiment 90.—Crystallized Sulphur.<sup>1</sup>** *Materials:* Sulphur (roll and flowers), Hessian crucible, carbon disulphide, evaporating dish.

(a) *Monoclinic.* Fix a folded filter paper firmly in a funnel, and place the funnel in a test tube which stands in a rack. Fill another test tube two thirds full of roll sulphur, heat it throughout its length at first, then melt the sulphur and quickly pour it upon the filter paper. Let it cool until crystals appear below the surface, then pour out the remaining melted sulphur. Observe and record the properties of the crystals, especially the shape, size, color, luster, brittleness, and any other characteristic property. Allow the best crystals to remain undisturbed for a day or two; then examine again, and record any marked changes.

(b) *Orthorhombic.* Put 3 grams of roll sulphur in a test tube and add about 10 cubic centimeters of carbon disulphide — remember the **precaution** to be observed in using this liquid (see Exp. 84). Shake until most of the sulphur is dissolved, then filter the solution into an evaporating dish to crystallize. It is advisable, and often absolutely necessary, to stand the dish in the hood or out of doors, where there is no flame and where the offensive vapor will be quickly removed. Watch the crystallization toward the end, and, if perfect crystals form, remove them with the forceps (see Fig. 49). Allow the

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<sup>1</sup> See Appendix, § 3 (3), (5).

liquid to evaporate almost entirely, then remove and dry the crystals. Examine them as in (a) and record their properties.

**EXERCISES:**

- (1) Tabulate the essential results in (a) and (b).
- (2) Make an outline sketch of an orthorhombic crystal of sulphur.

**Experiment 91. — Combining Power of Sulphur.** *Materials:* Sulphur, deflagrating spoon, bottle, iron powder, hydrochloric acid.

(a) Set fire to a little sulphur in a deflagrating spoon, and lower the spoon into a bottle. *Cautiously* waft the fumes toward the nose, and observe and describe the odor. The product is a mixture of two oxides of sulphur. What does their formation show about the combining power of sulphur?

(b) Repeat Experiment 34.

Results similar to that in (b) are obtained with copper and other metals. Draw a general conclusion regarding the power of sulphur to combine with metals.

**Experiment 92. — Sulphur and Matches.**

- (a) Examine a sulphur match. Do you detect any sulphur? Where?
- (b) Light a sulphur match, and observe the entire action, as far as the sulphur is concerned. Describe it.
- (c) What is the function of the sulphur in a burning match?

**Experiment 93. — Preparation of Hydrogen Sulphide.** *Materials:* Ferrous sulphide, dilute hydrochloric acid, three bottles, three glass plates, stoppered bottle, litmus paper. Use the same *apparatus* as in Experiment 38.

**Precaution.** *Hydrogen sulphide is a poisonous gas and has an offensive odor. It should not be inhaled. Perform in the hood all experiments evolving hydrogen sulphide.*

(a) Construct and arrange an apparatus like that shown in Figure 104. Fill the test tube, A, one third full of coarsely powdered ferrous sulphide, insert the stopper tightly, pour enough hydrochloric acid through the safety tube to cover the contents of the test tube. Hydrogen sulphide gas is rapidly evolved. If the evolution of gas slackens or stops, warm gently or add more hydrochloric acid. Collect three bottles, removing each as soon as full and covering with a glass plate. Set aside until needed.

(b) As soon as the last bottle of gas has been removed and covered, put in its place a bottle one fourth full of water. Adjust its height (by wooden blocks or by lowering the generator) so that the end of the delivery tube reaches to the bottom of the bottle. Continue to pass the gas into the water, by heating the test tube if necessary. The gas will be absorbed by the water, forming **hydrogen sulphide water**. Preserve it in a stoppered bottle for Experiment 95.

Proceed at once with next experiment.

**Experiment 94.—Properties of Hydrogen Sulphide Gas.**

Study as follows the hydrogen sulphide gas prepared in Experiment 93:—

(a) Waft a *little* of the gas cautiously toward the nose, and describe the odor. This is characteristic of hydrogen sulphide, and is a decisive test. Has the gas color?

(b) Test the gas from the same bottle with both kinds of moist litmus paper. Is it acid, alkaline, or neutral?

(c) Bring a lighted match to the mouth of the same bottle. Observe the properties of the flame as in previous experiments. Observe cautiously the odor of the product of the burned gas; to what compound is the odor due? What, then, is *one* component of hydrogen sulphide?

(d) Burn another bottle of hydrogen sulphide and hold a cold bottle over the burning gas. What additional experimental evidence does this result give regarding the composition of hydrogen sulphide?

(e) Repeat any of the above with the remaining bottle of gas.

**EXERCISES:**

(1) Summarize the properties of hydrogen sulphide gas.

(2) State the experimental evidence of its composition.

**Experiment 95.—Preparations and Properties of some Sulphides.** *Materials:* Hydrogen sulphide water prepared in Experiment 93, clean copper wire, clean sheet lead, bright silver coin, lead oxide (litharge); solutions of lead nitrate, arsenic trioxide (in hydrochloric acid), tartar emetic, zinc sulphate.

(a) Shake the bottle of hydrogen sulphide water prepared in Experiment 93 (or a similar solution), and hold successively at the mouth or in the neck of the bottle (1) a clean copper wire, (2) a bright strip of lead, and (3) an untarnished silver coin. Describe the result in each case. These compounds are sulphides of the respective metals.

(b) Put a little litharge—the brownish yellow oxide of lead—in a test tube, cover it with hydrogen sulphide water, and warm gently. The product is lead sulphide. Describe it. Explain the change.

(c) Add hydrogen sulphide water to lead nitrate solution. The product is lead sulphide. Observe the color.

(d) Proceed as in (c) with the arsenic solution. Observe the color of the arsenic sulphide.

(e) Proceed as in (c) with the tartar emetic solution. Tartar emetic is a compound of antimony. Observe the color of the antimony sulphide.

(f) Proceed as in (c) with the zinc sulphate solution. Observe the color of the zinc sulphide.

**Experiment 96.—Preparation of Sulphur Dioxide.** *Materials:* Sodium sulphite, concentrated sulphuric acid, litmus paper, three bottles, two glass plates, stick of wood, pink flower. The *apparatus* is constructed, arranged, and used as in Experiment 41, with one exception. The safety tube must be replaced by a dropping tube made thus: Cut off the top of a thistle tube about 2.5 centimeters (1 inch) below the juncture of the stem and cup, slip a thick rubber tube (5 centimeters, 2 inches, long) over one end of the stem, attach a Mohr's pinchcock to the rubber tube, and connect the tube with the cup.

(a) Put about 10 grams of sodium sulphite in the large test tube, cover with water, and insert the stopper with its tubes. Adjust the apparatus as shown in Figure 104. Fill the cup with concentrated sulphuric acid, press the pinchcock a little, and let the acid flow *drop by drop* upon the sodium sulphite. Sulphur dioxide gas is evolved and passes into the bottle, which should be removed when full, as previously described. Moist blue litmus paper held at the mouth of the bottle will show when the latter is full. Collect two bottles of gas, cover each with a glass plate, and set aside until needed.

(b) As soon as the second bottle of gas has been removed and covered, put in its place a bottle one fourth full of water. Adjust its height (if necessary) by wooden blocks, so that the end of the delivery tube is just above the surface. Continue to add the acid *drop by drop*, at intervals, and the gas will be absorbed by the water. Shake the bottle occasionally.

Meanwhile study the gas already collected.

**Experiment 97.—Properties of Sulphur Dioxide Gas.**

Proceed as follows with the gas prepared in Experiment 96 (a) :—

(a) Observe and state the most obvious physical properties, e.g. color, odor (cautiously), density.

(b) Hold a blazing stick in a bottle of the gas. Will the gas burn or support combustion? What previously acquired facts would have enabled you to predict this result?

(c) Pour water into the same bottle of sulphur dioxide until half full, cover with the hand, and shake. What is the evidence of solution? Is the resulting liquid acid, alkaline, or neutral?

(d) Moisten a pink flower with a few drops of water, hang it in the remaining bottle of sulphur dioxide, holding it in place by putting the stem between the glass and a cork. Observe and describe any change in the color of the flower. What is this operation called?

**Experiment 98.—Properties of Sulphurous Acid.**

Test as follows the solution of sulphurous acid prepared in Experiment 96 (b) :—

(a) Taste *cautiously*, and describe the result.

(b) Apply the litmus test, and state the result.

(c) Pour a few drops of concentrated sulphuric acid into the bottle. What gas is liberated?

**Experiment 99.—Action of Sulphuric Acid with Organic Matter.**

**Materials :** Concentrated sulphuric acid, sheet of white paper, sugar, starch, stick of wood.

(a) Write some letters or figures with dilute sulphuric acid on a sheet of white paper, and move the paper back and forth over a low flame, taking care not to set fire to the paper. As the water evaporates the dilute acid becomes concentrated. Observe and describe the result. Paper is largely a compound of carbon, hydrogen, and oxygen, and the hydrogen and oxygen are present in the proportion to form water. Explain the general chemical change in this experiment.

(b) Fill a test tube one fourth full of sugar, add an equal bulk of water, stand the test tube in the rack, and add *cautiously* several drops of concentrated sulphuric acid. If there is no decided result, add more acid. What is the black product? Compare the final result with that obtained in Experiment 59 (b). Is the chemical action the same in

each experiment? Are the statements made in (a) about paper also true of sugar?

(c) Repeat (b), using powdered starch instead of sugar. Describe the result. How does the result resemble that in (b) and in Experiment 59 (a)? Predict the components of starch. In what simple way may the prediction be verified?

(d) Stand a stick of wood in a test tube one fourth full of concentrated sulphuric acid. Allow it to remain in the acid for fifteen minutes, then remove the stick and wash off the acid. Describe the change in the stick. Does it resemble that in (a), (b), and (c), and in Experiment 59 (a)?

**Experiment 100.—Test for Sulphuric Acid and Sulphates.**

*Materials:* Sulphuric acid, sodium sulphate, barium chloride solution, calcium sulphate, charcoal, powdered charcoal, blowpipe, silver coin.

(a) Repeat Experiment 12 (c) with sulphuric acid and with sodium sulphate solution.

(b) Repeat Experiment 79 I (b) with calcium sulphate instead of sodium sulphate.

**EXERCISES:**

(1) State briefly the test for sulphuric acid and soluble sulphates. For insoluble sulphates.

(2) How can a sulphate be distinguished from a sulphite?

SILICON AND BORON.

**Experiment 101.—Preparation and Properties of Silicic Acid.**

*Materials:* Sodium silicate solution, hydrochloric acid, evaporating dish, gauze-covered ring.

Add dilute hydrochloric acid to a test tube half full of sodium silicate solution, and shake. The jellylike precipitate is silicic acid. Rub some between the fingers and describe the result. Evaporate the precipitate to dryness in a porcelain dish which stands upon a gauze-covered ring in the hood. As the mass hardens, stir it with a glass rod. Toward the end, add more hydrochloric acid and evaporate to complete dryness. Then heat strongly for five minutes. The residue is silicon dioxide mixed with chlorides of sodium and potassium. Rub some between the fingers or across a glass plate. Is any grit detected? State the chemical changes which occur in changing sodium silicate into silicon dioxide.

**Experiment 102.—Tests with Borax Beads.** *Materials:* Powdered borax, platinum test wire (see Int. § 5 (4)), solutions of cobalt nitrate and copper sulphate, manganese dioxide.

Make a small loop on the end of the platinum test wire, moisten it, and dip it into powdered borax. Heat it in the flame, rotating it slowly; at first the borax swells, but finally shrinks to a small, transparent bead. If the bead is too small add more borax and heat again. After use, the bead may be removed by dipping it, white hot, into water; the sudden cooling shatters the bead, which may then be easily rubbed or scraped from the wire.

(a) *Cobalt Compounds.* Touch a transparent borax bead with a glass rod which has a drop of cobalt nitrate solution on the end. Heat the bead in the oxidizing flame. Observe the color when cold. If it is black melt a little more borax into the bead; if faintly colored, moisten again with the cobalt solution. The color is readily detected by looking at the bead against a white object in a strong light, or by examining it with a lens. When the color has been definitely determined, heat again in the reducing flame. Compare the color of the cold bead with the previous observation.

(b) *Copper compounds.* Make another transparent bead, moisten it with copper sulphate solution and heat it first in the oxidizing flame, and then in the reducing flame. Compare the colors of the cold beads, and draw a conclusion.

(c) *Manganese Compounds.* Make another transparent bead, touch it with a minute quantity of manganese dioxide, and proceed as in (b). Compare the colors of the cold beads, and draw a conclusion.

(d) Tabulate the results of this experiment.

#### EXERCISE:

Draw a Bunsen flame, showing the reducing and oxidizing parts.

**Experiment 103.—Preparation and Properties of Boric Acid and the Test for Boron.** *Materials:* Borax, alcohol, evaporating dish, concentrated hydrochloric acid.

In a test tube half full of boiling water, dissolve 10 grams of powdered borax. Add about 5 cubic centimeters of concentrated hydrochloric acid to this hot solution, and let the whole cool. Crystals of boric acid will separate. Filter. Describe the crystals.

Put some of the crystals in an evaporating dish, add a little alcohol,

## Experiments.

and set fire to the solution. Observe the color of the flame. It is caused by a complex compound of boron, and is the test for this element.

### PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH.

#### **Experiment 104.—Some Properties of Phosphorus.**

(a) Smell of the head of a phosphorus-tipped match. Describe the odor.

(b) Rub the head of a phosphorus-tipped match in a dark place, and observe and describe the result.

(c) The most striking property of phosphorus is the readiness with which it lights and burns in air. This property is too dangerous to try in the laboratory. Read about it in the text book. What application is made of this property? Why?

#### **Experiment 105.—Test for Arsenic.**

Repeat Experiment 95 (d).

#### **Experiment 106.—Test for Antimony.**

Repeat Experiment 95 (e).

#### **Experiment 107.—Test for Bismuth. Materials:** Bismuth, *aqua regia*.

Prepare a solution of bismuth chloride by heating the metal with *aqua regia*. Fill the test tube half full of water, and describe the result. The product is bismuth oxychloride. How is it related to bismuth chloride?

## SODIUM.

#### **Experiment 108.—Properties of Sodium. Materials:** Sodium, pneumatic trough filled with water as usual, litmus paper, filter paper, tea lead.

**Precaution.** Observe the precautions as in Experiment 24.

(a) Examine a small piece of sodium, and record its most obvious physical properties, *e.g.* color, luster, whether hard or soft, etc.

(b) Repeat Experiment 24 (except (e)).

#### **ANSWER :**

- (1) Is sodium heavier or lighter than water?
- (2) What properties show that it is a metal?

- (3) Is it harder or softer than most metals?
- (4) What is the test for sodium?

**Experiment 109.—Preparation and Properties of Sodium Hydroxide.** *Materials:* Sodium carbonate, lime, zinc sulphate solution, iron (or tin) dish, file.

Dissolve 25 grams of sodium carbonate in 150 cubic centimeters of water and heat gently in an iron dish (an ordinary iron spider is well adapted for this work). Meanwhile slake 10 grams of lime by adding just enough water to make a milky liquid — "milk of lime." Add the milk of lime to the sodium carbonate solution and boil for several minutes, stirring constantly with a file. Let the precipitate settle, remove a little liquid with a small tube, and if it effervesces with hydrochloric acid, add more milk of lime and boil; if not, pour the liquid into a convenient vessel, let it stand for a few minutes or until the solid settles; then pour the liquid down a glass rod (see Int. § 6 (1)) into a bottle. This solution of sodium hydroxide may be evaporated to dryness, and the solid product tested and the remainder preserved, or the solution may be tested at once as follows:—

- (a) Rub a little between the fingers and describe the feeling.
- (b) Apply the litmus test. Is it acid or alkaline? Is it markedly so?
- (c) Add a little to a zinc sulphate solution, and shake. The precipitate is zinc hydroxide. Describe it. Now add an excess of sodium hydroxide, and shake. Describe the result. The excess of sodium hydroxide forms soluble sodium zincate. This behavior of zinc compounds is the **test for an hydroxide**.
- (d) How do sodium compounds affect a colorless flame? Try it, if in doubt.

**Experiment 109 a.—Preparation and Properties of Sodium Bicarbonate.** *Materials:* Ammonium carbonate, ammonium hydroxide, sodium chloride, carbon dioxide generator.

Put 8 grams of powdered ammonium carbonate and 75 cubic centimeters of ammonium hydroxide into a bottle; add about 35 grams of fine sodium chloride, cork the bottle, and shake the mixture vigorously until most of the solid has dissolved. Filter the liquid into a large test tube. Put considerable marble into the generator, and pass carbon dioxide through the solution from thirty to forty-five minutes or until a precipitate begins to form. Then cork the test tube and let it stand an hour or more to allow the sodium bicarbonate to settle out of the solu-

tion. Filter, and wash quickly with a little cold water. Dry the precipitate between filter paper. Describe it. Subject portions to the flame test for sodium and the usual test for a carbonate. State the result.

### POTASSIUM.

**Experiment 110.—Properties of Potassium.** *Materials:* Potassium, pneumatic trough filled as usual, litmus paper.

**Precaution.** *Observe the same precaution as in using sodium.*

(a) Examine a very small piece of freshly cut potassium, and record its most obvious physical properties. Touch it slightly. Does it suggest caustic potash and soda?

(b) Drop a small piece of potassium on the water in a pneumatic trough. Stand just near enough to see the action. Describe the action. How does it differ from the action of sodium? Test the water as in Experiment 24 (*d*).

From what has already been learned about sodium and potassium, predict the main chemical change observed in (b).

#### ANSWER :

- (1) Is potassium heavier or lighter than water?
- (2) What properties suggest that it is a metal?
- (3) How does it resemble and differ from sodium?
- (4) How does potassium color a flame?
- (5) What is the test for potassium?

**Experiment 111.—Preparation and Properties of Potassium Hydroxide.** *Materials:* Potassium carbonate, lime, zinc sulphate solution, iron (or tin) dish, file.

Proceed as in Experiment 109, but use potassium carbonate instead of sodium carbonate. Test as in the case of sodium hydroxide.

**Experiment 112.—Preparation and Properties of Potassium Carbonate.** *Materials:* Cream of tartar, wood ashes, litmus paper, hydrochloric acid, iron sand bath pan, mortar and pestle.

(a) Heat strongly 5 grams of cream of tartar—acid potassium tartrate—in an iron pan in the hood from fifteen to twenty minutes. Grind this solid with water in a mortar, and filter. Test the filtrate (1) with both kinds of litmus paper, (2) for potassium, and (3) for a carbonate. Record the results.

(b) Fill a test tube half full of wood ashes, add half the volume of water, shake, and warm gently. Filter, and test the filtrate as in (a). If test (3) is not decisive, repeat the experiment on a larger scale. Record the results.

(c) Expose a little potassium carbonate to the air for an hour or more. Describe the result. How does its behavior compare with that of sodium carbonate under the same conditions?

**ANSWER :**

- (1) What is the source of cream of tartar?
- (2) What do (a) and (b) show about the distribution of potassium? Of its assimilation by plants?
- (3) What is the literal meaning of the word *potash*?

**Exercises for Review.**

1. What does potassium chlorate yield when heated?
2. Does potassium chlorate dissolve readily in cold water? In hot water?
3. What is formed by heating potassium bromide with manganese dioxide and sulphuric acid?
4. Apply question 3 to potassium iodide.
5. What happens to potassium hydroxide when exposed to air? To potassium carbonate?
6. Of what important mixture is potassium nitrate an ingredient?

**COPPER.**

**Experiment 113.—Physical Properties of Copper.**

Examine several forms of copper—wire, sheet, filings, etc.—and state the most obvious physical properties.

**ANSWER :**

- (1) Is copper a good conductor of heat? Of electricity? On what evidence is your answer based?
- (2) Is copper ductile? Malleable? Brittle? Tough? Hard or soft?
- (3) What happens to copper when heated? When exposed to the air?

## Experiments.

**Experiment 114.—Tests for Copper.** *Materials:* Copper wire, copper sulphate solution, ammonium hydroxide, acetic acid, potassium ferrocyanide solution.

(a) Heat a copper wire in the Bunsen flame. The color is characteristic of copper and its compounds, though not a conclusive test, since the same color is produced by other substances.

(b) Add a few drops of ammonium hydroxide to copper sulphate solution, and observe the result; now add an excess of ammonium hydroxide. The blue solution is a characteristic and decisive test for copper.

(c) Add to a test tube one fourth full of water an equal volume of copper sulphate solution, and shake; then add a few drops of acetic acid and of potassium ferrocyanide solution. The brown precipitate is copper ferrocyanide.

**Experiment 115.—Interaction of Copper with Metals.** *Materials:* Copper wire, iron nail, zinc, solutions of copper sulphate and any mercury compound.

(a) Put a clean copper wire into a solution of any mercury compound. After a short time, remove the wire and wipe it with a soft cloth or paper. Describe the change. What has become of some of the copper?

(b) Put in separate test tubes half full of copper sulphate solution a bright iron nail and a strip of clean zinc. After a short time remove the metals and examine them. What is the deposit? What has become of some of the zinc and iron? Does the final color of the solution indicate any chemical change? How would you prove the answer to the last question?

### Exercises for Review.

1. What happens to a crystal of copper sulphate when heated?
2. You are given a blue solution supposed to be copper sulphate. State how you would prove it.
3. What are formed by the interaction of copper and nitric acid?
4. What color have many copper compounds?
5. "Brass is an alloy of copper." State how you would prove this.

### SILVER AND GOLD.

**Experiment 116.—Preparation of Silver.** *Materials:* (a) Silver nitrate solution, mercury, evaporating dish; (b) ten-cent piece,

concentrated nitric acid, hydrochloric acid, sulphuric acid, zinc, evaporating dish, charcoal, sodium carbonate, blowpipe.

Prepare silver by one or both of the following methods : —

(a) Fill a porcelain dish half full of silver nitrate solution, and add a few drops of mercury. Allow the whole to stand undisturbed for a day or more, and then examine. The delicate crystals attached to the mercury are silver. Pick them out with the forceps, wash well with water, and preserve them for Experiment 117.

(b) Dissolve a ten-cent piece in 10 cubic centimeters of concentrated nitric acid, dilute with an equal volume of water, and add hydrochloric acid until the precipitation is complete. Let the precipitate settle. Then filter, and wash until the filtrate is neutral. If convenient, let the precipitate dry; if not, scrape half from the opened paper with a knife, put it in a porcelain dish, cover with dilute sulphuric acid, and add a piece of zinc; put the other half in a cavity at the end of a piece of charcoal, cover with sodium carbonate, and reduce it with a blowpipe flame. In the first case, the silver will collect as a grayish powder; remove any excess of zinc, filter, wash with water and dry the residue. It may be preserved as a powder, or fused into a bead with a blowpipe flame. In the second case, minute globules of silver will appear on the charcoal; scrape them together and fuse into a single bead. Preserve it.

#### **Experiment 117.—Properties of Silver.**

Examine the silver formed in Experiment 116, and state briefly its most obvious properties.

#### **Experiment 118.—Test for Silver.**

Devise a test for combined silver, based upon previous experiments. Verify it.

#### **Exercises for Review.**

1. What is formed by the interaction of silver nitrate and potassium chloride? Potassium bromide? Potassium iodide? How do the products differ?
2. What caused the blue filtrate in Experiment 116 (b)? What metal besides silver does a ten-cent piece contain?
3. What compound is formed when silver tarnishes?
4. What is the test for a chloride?

**Experiment 119.—Interaction of Gold and Aqua Regia and the Test for Gold.** *Materials:* Gold leaf, concentrated nitric and hydrochloric acids, stannous chloride solution.

Prepare a solution of gold chloride according to Experiment 58, using as small a volume of the acids as possible. Dilute with water, and then slowly add a dilute solution of stannous chloride. A precipitate is produced, varying in color from faint purple to black according to the conditions. This precipitate is supposed to be finely divided gold, and is called *Purple of Cassius*; its formation is the test for gold.

#### CALCIUM.

**Experiment 120.—Tests for Calcium.**

- (a) Subject calcium chloride to the flame test. Record the result.
- (b) Repeat Experiment 12 (d).

**Experiment 121.—The "Setting" of Plaster of Paris.** *Materials:* Plaster of Paris, block of wood.

Mix a little plaster of Paris with enough water on a block of wood to form a thin paste. Let it stand undisturbed for a few minutes, and then examine. Describe the change. How is this property utilized?

**Experiment 121 a.—Per Cent of Water of Crystallization in Crystallized Calcium Sulphate.** *Materials:* Porcelain dish, crystallized calcium sulphate (selenite).

Weigh accurately a clean, dry porcelain dish. Coarsely powder about 10 grams of crystallized calcium sulphate, put it into the dish, and weigh the dish and contents accurately. Stand the dish on a gauze-covered support and heat strongly about fifteen minutes. Cool, and weigh. Heat again intensely about five minutes; cool, and weigh. If the weight is not the same as before, heat a third time, cool, and weigh. Subtract the last weight from the weight of the dish and contents. The loss is the weight of the water of crystallization. Calculate the per cent of water of crystallization in the calcium sulphate. Submit the result.

#### Exercises for Review.

1. Describe calcium chloride. How does it act when exposed to the air? How would you show that it (a) contains calcium and (b) is a chloride?

2. Describe lime. What effect does water have upon it?
3. What compounds are produced by the interaction of calcium carbonate and hydrochloric acid?
4. What is limewater? Milk of lime?
5. What is formed when carbon dioxide is passed into limewater? Into sodium hydroxide?
6. What compounds are formed by heating calcium carbonate?
7. What happens when an excess of carbon dioxide is passed into limewater?

### STRONTIUM.

#### Experiment 122.—Test for Strontium.

Dip a platinum test wire (or a glass rod) into a solution of strontium nitrate, and hold it in the Bunsen flame. Describe the result, after several trials.

#### Experiment 123.—Red Fire. *Materials:* Strontium nitrate, powdered potassium chlorate, powdered shellac, iron pan or brick.

Mix carefully small and equal (in bulk) quantities of the three substances on a sheet of paper. Place the mixture on a sand-bath pan or a brick in the hood, and light it with a Bunsen burner. Describe the result.

### BARIUM.

(*Compounds of Barium are Poisonous.*)

#### Experiment 124.—Tests for Barium.

(a) Repeat Experiment 122, using a solution of barium chloride or barium nitrate. Be sure the test wire (or rod) is clean. Describe the result.

(b) Devise a test. (Suggestion. What is the test for a sulphate?)

#### Experiment 125.—Green Fire.

Repeat Experiment 123, using barium nitrate instead of strontium nitrate.

#### Experiment 125 a.—Per Cent of Water of Crystallization in Crystallized Barium Chloride. *Materials:* Porcelain dish, crystallized barium chloride.

Repeat Experiment 121 a, using 5 grams of crystallized barium chloride instead of calcium sulphate.

## Experiments.

### MAGNESIUM.

#### **Experiment 126.—Properties of Magnesium.**

Examine a piece of magnesium and state briefly its most obvious properties.

**Experiment 127.—Tests for Magnesium.** *Materials:* Solutions of magnesium sulphate (or chloride), ammonium chloride, ammonium hydroxide, disodium phosphate, and cobaltous nitrate; magnesium oxide, charcoal, blowpipe.

(a) To a solution of magnesium sulphate (or chloride) add successively solutions of ammonium chloride, ammonium hydroxide, and disodium phosphate. A precipitate of ammonium magnesium phosphate is formed. It is voluminous at first, but finally crystalline. It is soluble in acids. Try it.

(b) Put a little powdered magnesium oxide in a cavity at the end of a piece of charcoal, moisten with water, and heat intensely in a blowpipe flame. Cool, and moisten with a drop of cobaltous nitrate solution. Heat again, and when cool observe the color. If the experiment has been conducted properly, a pink or pale flesh-colored residue coats the charcoal. Describe the result.

### Exercises for Review.

1. What compound is formed by burning magnesium in air or in oxygen? Describe it.
2. How was magnesium utilized in the discovery of argon?

### ZINC.

#### **Experiment 128.—Properties of Zinc.**

Examine a piece of zinc and record its most obvious properties.

#### ANSWER :

1. What happens to zinc when it is heated? Describe and name the product.
2. Is zinc hard or soft? Malleable? Ductile? Brittle? Tough? Does it melt readily?

**Experiment 129.—Tests for Zinc.** *Materials:* Zinc oxide, cobaltous nitrate solution, charcoal, blowpipe.

(a) Recall or devise a simple test for combined zinc. (Suggestion. See Exp. 109 (c).)

(b) Recall or repeat the action of zinc when heated in the oxidizing flame. (See Exp. 79 II (a).)

(c) Fill a small cavity at one end of a piece of charcoal with zinc oxide, moisten with water, and heat strongly in the blowpipe flame. Cool, and moisten with a drop of cobaltous nitrate solution, then heat again. Cool and examine. A green incrustation is caused by zinc compounds.

**Experiment 130. — Interaction of Zinc and Metals.** *Materials:* Sheet zinc, solutions of copper sulphate, lead nitrate, mercurous nitrate.

(a) Repeat Experiment 115 (b) with zinc.

(b) Repeat (a) using lead nitrate solution.

(c) Repeat (a) using the mercury salt solution. Examine after a short time, and describe. What is amalgamated zinc, and for what is it used?

#### Exercises for Review.

1. What are formed by the interaction of zinc and sulphuric acid? Of zinc and nitric acid?

2. What is formed by the interaction of a zinc salt and a little sodium hydroxide solution? An excess of the alkali?

### CADMIUM.

#### Experiment 131. — Test for Cadmium.

Add hydrogen sulphide water to a test tube half full of cadmium chloride solution. The precipitate is cadmium sulphide. Describe it. Let it settle, pour off most of the liquid, fill the test tube half full with dilute sulphuric acid, and warm. Describe the result.

### MERCURY.

*(Mercury and its Compounds are Poisonous.)*

#### Experiment 132. — Properties of Mercury.

(a) Pour a drop or two of mercury into an evaporating dish. Examine the mercury, and state its characteristic properties. Agitate the dish, and describe the result. Why is mercury called "quicksilver"?

(b) Lift carefully a bottle of mercury. Estimate the specific gravity. Verify the estimate by consulting a book.

## Experiments.

### **Experiment 133.—Tests for Mercury.**

- (a) What is a simple test for free mercury?
- (b) Recall or devise a test for combined mercury. Verify it. (Suggestion. See Exp. 115.)

### **Experiment 134.—Properties of Mercurous and Mercuric Compounds.** *Materials:* Solutions of mercurous and mercuric nitrate; hydrochloric acid, ammonium hydroxide.

(a) *Mercurous.* Add a few drops of hydrochloric acid to a little mercurous nitrate solution. The white precipitate is mercurous chloride. Note its insolubility in water and in dilute hydrochloric acid. Add an excess of ammonium hydroxide. The black precipitate is mercurous ammonium chloride. Its formation is a delicate test for mercury in mercurous compounds.

(b) *Mercuric.* Add a few drops of hydrochloric acid to a little mercuric nitrate solution. Compare the result with that in (a). Add a few drops of ammonium hydroxide, or enough to produce a decided change. Compare with (a). The precipitate is mercuric ammonium chloride.

### **Exercises for Review.**

1. Describe the effect of heat on red oxide of mercury. What historical interest has this experiment?
2. What practical use has mercury?
3. What are amalgams?
4. What action has mercury upon gold?

## ALUMINIUM.

### **Experiment 135.—Properties of Aluminium.**

- (a) Examine a piece of aluminium, and observe its properties. Has it any "spring" like brass? Is it ductile, malleable, soft, hard, tough, brittle? Will it melt in the Bunsen flame? Try it.
- (b) Compare roughly the weight of a piece of sheet aluminium with a piece of pasteboard or glass having approximately the same volume.
- (c) Find the specific gravity by the method used in Experiment 88 (b).

### **Experiment 136.—Action of Aluminium with Acids and Alkalies.** *Materials:* Aluminium, sulphuric acid, hydrochloric acid, sodium hydroxide solution.

(a) Add a small piece of aluminium to separate test tubes containing dilute sulphuric acid and concentrated hydrochloric acid. Warm, if necessary. Describe the action. Test the gas evolved. What compound is formed in each case?

(b) Add a small piece of aluminium to a test tube half full of dilute sodium hydroxide solution, and boil. Test any gas evolved. If only a little gas is liberated, attach a simple delivery tube and collect the gas over water.

Other acids and alkalies act similarly. Draw a general conclusion from this experiment.

**Experiment 137.—Preparation and Properties of Aluminium Hydroxide.** *Materials:* Solutions of alum, sodium hydroxide, ammonium sulphide, and cochineal; hydrochloric acid and ammonium hydroxide.

(a) Add slowly a little sodium hydroxide solution to a test tube half full of alum solution. The gelatinous precipitate is aluminium hydroxide. Now add an excess of the alkali to one half, and dilute hydrochloric acid to the other. Describe the results.

(b) Add a little solution of ammonium sulphide to a solution of alum. Describe the result. The precipitate is not a sulphide, but aluminium hydroxide, because aluminium forms no sulphide in the wet way.

(c) Add a little alum solution to a dilute solution of cochineal, then add ammonium hydroxide. The colored product is called carmine lake. Filter, and compare the color of the filtrate with that of the carmine lake.

**Experiment 138.—Tests for Aluminium.** *Materials for (c):* Aluminium sulphate; cobaltous nitrate solution, blowpipe, charcoal.

(a) What is a simple test for metallic aluminium?

(b) Recall or devise a test for combined aluminium. Verify it. How can aluminium compounds be distinguished from those of zinc?

(c) Heat a little aluminium sulphate on charcoal in the blowpipe flame. Cool, and moisten with a drop of cobaltous nitrate solution. Heat again, and if the operation has been conducted properly, a blue residue will coat the charcoal. This color is characteristic of aluminium compounds. Compare this result with the action of other metallic compounds under similar circumstances.

## Experiments.

**Experiment 139.—Preparation and Properties of Common Alum.** *Materials for (a):* Aluminium sulphate, potassium sulphate, evaporating dish.

(a) Dissolve about 10 grams of aluminium sulphate in the least possible amount of hot water. Dissolve 3 grams of potassium sulphate in the same way. Mix the clear, hot, saturated solutions in an evaporating dish, and allow the solution to cool undisturbed. Crystals of potassium alum will be deposited. Remove the best ones; dry and examine. Describe them, giving color, luster, size, and crystal form.

(b) Prove by actual tests that (1) they are a sulphate, and (2) they contain aluminium and water of crystallization.

### TIN.

**Experiment 140.—Properties of Tin.** Examine a piece of tin, and state its most obvious properties. Is it malleable, soft, hard, tough, brittle? Will it melt in the Bunsen flame? Try it.

**Experiment 141.—Action of Tin with Acids.** *Materials:* Tin, concentrated nitric and hydrochloric acids.

(a) Put a small piece of tin in a test tube, cover with concentrated hydrochloric acid, add a little water, and heat—*in the hood*. Heat gently at first, and when action begins regulate the heat accordingly. Most of the tin disappears, soluble stannous chloride being formed. Save this solution for Experiment 142.

(b) Treat a small piece of tin with concentrated nitric acid—*in the hood*. It is advisable to stand the test tube in the rack or in a bottle as soon as the action begins. The white, amorphous product is metastannic acid. How does the action of nitric acid on tin differ from and resemble its action on other metals, zinc, for example?

**Experiment 142.—Tests for Tin.** *Materials for (c):* Solutions of mercuric chloride and stannous chloride.

- (a) What is a simple test for metallic tin?
- (b) Recall or repeat the action of tin when heated in a blowpipe flame.

(c) Add a few drops of mercuric chloride solution (*poison*) to a little of the stannous chloride solution prepared in Experiment 141. The white precipitate is mercurous chloride. Add a little more stannous chloride

solution and heat gently. The mercurous chloride is reduced finally to mercury, which appears as a grayish powder.

**Experiment 143.—Deposition of Tin.**

Put a strip of zinc in a slightly acid solution of stannous chloride. Examine after a short time. The tin will be found adhering to the zinc as a grayish black deposit; sometimes bright scales are also seen. What has become of the zinc?

LEAD.

**Experiment 144.—Properties of Lead.**

- (a) Examine a piece of freshly cut lead and state its most obvious physical properties.
- (b) Estimate its specific gravity. Verify your estimate by consulting a book.
- (c) Draw a piece of lead across a sheet of white paper, and describe the result.
- (d) Is lead easily melted? Try it.

**ANSWER :**

- (1) What happens to lead when exposed to the air?
- (2) What properties adapt lead for its extensive use?
- (3) What is "black lead"?
- (4) Is there lead in a lead pencil?

**Experiment 145.—Tests for Lead.** *Materials for (c), (d), (e):* Lead nitrate and potassium dichromate solutions, sulphuric acid, hydrochloric acid.

- (a) Recall or repeat the reduction of lead oxide in the blowpipe flame. (See Exp. 79.)
- (b) Recall or repeat the action of hydrogen sulphide with the solution of a lead compound. (See Exp. 95 (c).)
- (c) Add dilute hydrochloric acid to a little lead nitrate solution until precipitation ceases. Note the insolubility of the lead chloride which is formed. Boil some of the precipitate with considerable water. Describe the action. This is characteristic of lead chloride and permits its separation from the chlorides of silver and of mercury (in the *-ous* condition).

(d) Add dilute sulphuric acid to a little lead nitrate solution until precipitation ceases. The precipitate is lead sulphate. Observe its properties. Is it soluble in hot water? Try it.

(e) Repeat (d), using potassium dichromate solution instead of sulphuric acid. The precipitate is lead chromate. Describe it, especially the color.

**Experiment 146.—Deposition of Lead.**

Repeat Experiment 130 (b).

**Experiment 147.—Properties of Lead Oxides.** *Materials:* Lead monoxide, dioxide, and tetroxide, nitric acid.

(a) Examine the three oxides and tabulate their most obvious physical properties, stating the exact chemical name and formula and the popular name of each oxide.

(b) Recall the experiment in which lead was heated in the oxidizing flame, especially the color of the coating. What oxide of lead is thereby formed?

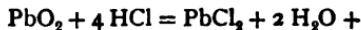
(c) Warm a little lead tetroxide with dilute nitric acid. The solid product is lead dioxide. Describe it.

**EXERCISES :**

(1) How might lead tetroxide be prepared?

(2) If lead tetroxide is heated strongly, lead monoxide is formed. What does this fact reveal about the stability of lead tetroxide?

(3) When lead dioxide and concentrated hydrochloric acid are mixed and heated, chlorine is evolved. Complete the equation —



How does this interaction resemble that of manganese dioxide and hydrochloric acid?

**Experiment 148.—Properties of Certain Lead Compounds.** *Materials:* Lead nitrate, lead carbonate, galena, taper, mortar and pestle.

(a) Put a crystal of lead nitrate in a test tube provided with a holder, hold in a horizontal position, and heat strongly in the upper part of the Bunsen flame. Describe the result. What is the most obvious product? After most of this product has passed out of the test tube, thrust well into the test tube a joss stick glowing on the

end. Describe the result. What other gas is present? The solid product is lead monoxide. Summarize the behavior of lead nitrate when heated.

(b) Examine lead carbonate, and state its most obvious properties. What is its common name? Prove that it is a carbonate and contains lead. (Suggestion. Treat with hydrochloric acid.)

(c) Examine a lump of galena, and state its most obvious properties. Pulverize it in a mortar. What additional property is revealed? Prove that it is a sulphide and contains lead. (Suggestion. See Exps. 93 and 145.)

#### CHROMIUM.

**Experiment 149.—Tests for Chromium.** *Materials:* Borax, chrome alum, potassium carbonate, potassium nitrate, acetic acid, nitric acid, sodium hydroxide solution, lead nitrate solution, potassium dichromate solution, platinum test wire, piece of porcelain, forceps.

(a) Prepare a borax bead (see Exp. 102), touch it with a minute quantity of chrome alum, and heat in both the oxidizing and reducing flame. Describe the result.

(b) Mix equal small quantities of potassium carbonate, potassium nitrate, and powdered chrome alum, place the mixture on a piece of porcelain, and hold it with the forceps in the upper Bunsen flame so that the mixture will fuse. A yellow mass, due to the presence of potassium chromate, results. If the color is not decided, dissolve the mass in water, add acetic acid, slowly at first, and boil to expel the carbon dioxide. Add a few drops of lead nitrate solution to a portion, and yellow lead chromate is precipitated. If the precipitate is white, it is lead carbonate, and shows that not all the potassium carbonate was decomposed, as intended.

(c) Add lead nitrate solution to potassium dichromate solution. Name and describe the precipitate. Try the solubility of the precipitate in acetic acid, dilute nitric acid, and sodium hydroxide. Describe the result.

**Experiment 150.—Properties of Chromates.** *Materials:* Potassium chromate and dichromate, concentrated hydrochloric acid, potassium hydroxide solution.

(a) Examine crystals of potassium chromate and dichromate, and state their characteristic properties. Make a dilute solution of each, and compare the colors. Save for (c) and (d).

- (b) State the properties of lead chromate.
- (c) Add a few drops of concentrated hydrochloric acid to the solution of potassium chromate prepared in (a), and observe the change in color. Describe it. Compare with the color of the potassium dichromate solution prepared in (a). Draw a conclusion.
- (d) Add potassium hydroxide solution to the solution of potassium dichromate prepared in (a) until a change of color is produced. Describe the color. Compare with the potassium chromate solution. Draw a conclusion.
- (e) The chromates are oxidizing agents. Add a few drops of concentrated hydrochloric acid to powdered potassium chromate and dichromate in separate test tubes. Chlorine is evolved. Where did it come from? By what general chemical change?

**Experiment 151.—Reduction of Chromates to Chromic Compounds.** *Materials:* Potassium dichromate solution, concentrated hydrochloric acid, alcohol.

Add to a few cubic centimeters of potassium dichromate solution a little concentrated hydrochloric acid and a few drops of alcohol. Warm gently. Two important changes occur. The chromate is *reduced* to chromic chloride which colors the solution green; the alcohol is oxidized to aldehyde, which is detected by its peculiar odor.

**Experiment 152.—Preparation and Properties of Chromic Hydroxide.** *Materials:* Ammonium sulphide, solutions of sodium hydroxide and chrome alum.

(a) Add a little sodium hydroxide solution to a solution of chrome alum. The precipitate is chromic hydroxide. Describe it. Add an excess of sodium hydroxide solution, and shake. Describe the result. Boil, and state the result.

(b) Add a little, and then an excess, of ammonium sulphide to a solution of chrome alum. Compare the result with that in (a). Does chromium form a sulphide?

#### ANSWER :

How can chromic hydroxide be distinguished from aluminium hydroxide?

**Experiment 153. — Properties of Chrome Alum.**

(a) Examine chrome alum and state its most obvious physical properties.

(b) Prove that chrome alum is a sulphate, and that it contains chromium and water of crystallization.

**MANGANESE.**

**Experiment 154. — Tests for Manganese.** *Materials for (b) and (c) :* Manganese dioxide, potassium carbonate, potassium nitrate, ammonium sulphide, manganese sulphate solution, hydrochloric acid, acetic acid, ammonium hydroxide.

(a) Subject a minute quantity of manganese dioxide to the borax bead test, and note the color of the bead after heating in each flame. (See Exp. 102.)

(b) Fuse, on a piece of porcelain, a little manganese dioxide mixed with potassium carbonate and potassium nitrate. The green mass is a test for manganese. It is due to the presence of potassium manganate.

(c) Add ammonium sulphide to manganese sulphate solution. The flesh-colored precipitate is manganese sulphide. Compare with other sulphides as to color (see Exp. 95). Divide it into two parts. Add hydrochloric acid to one, and acetic acid to the other, then add an excess of ammonium hydroxide to each. Draw a conclusion regarding the solubility of manganese sulphide.

**Experiment 155. — Oxidation with Potassium Permanganate.** *Materials :* Potassium permanganate, sulphuric acid, ferrous sulphate, filter paper.

(a) Add a few drops of sulphuric acid to a weak solution of *fresh* ferrous sulphate; then add, drop by drop, a dilute solution of potassium permanganate. Its color is changed, owing to the loss of oxygen; the latter converts the ferrous to ferric sulphate. The decomposition of the permanganate also causes the formation of potassium and manganese sulphates.

(b) Boil a piece of filter paper in a solution of potassium permanganate. Describe and explain the result.

## Exercises for Review.

1. Describe manganese dioxide. Name five elements in whose preparation manganese dioxide is used. Is manganese dioxide an oxidizing agent?
2. Describe potassium permanganate. What can be said of its solubility in water? In what previous experiment has it been used?
3. What is the formula of potassium permanganate? Does the formula suggest its oxidizing power?

## IRON.

**Experiment 156.—Properties of Iron.** *Materials:* Cast and wrought iron, steel, magnet, iron wire, iron powder.

- (a) Examine cast iron, wrought iron, and steel, and state their most obvious physical properties.
- (b) Try the action of a magnet on each. Describe the result.
- (c) Drop a pinch of iron powder into the Bunsen flame. Hold a piece of fine iron wire in the flame. Describe the results, and draw a conclusion.

**Experiment 157.—Properties of Ferrous Compounds.** *Materials:* Iron powder (or filings), hydrochloric acid, solutions of sodium hydroxide, potassium ferricyanide, potassium thiocyanate, potassium ferrocyanide.

Put a few grams of iron powder in a test tube, add about 10 cubic centimeters of dilute hydrochloric acid, and warm gently; ferrous chloride is formed (in solution). Proceed as follows: (1) Pour a little into a test tube one third full of sodium hydroxide solution. The precipitate is ferrous hydroxide. Watch the changes in color. To what are the changes due? (2) Add a second portion to potassium ferricyanide solution. The precipitate is ferrous ferricyanide. Describe it. (3) Add a third portion to potassium thiocyanate solution. If ferric salts are absent, no change results. (4) Add a fourth portion to potassium ferrocyanide solution. The precipitate is ferrous ferrocyanide. Describe it. Tabulate the results as described in the next experiment.

**Experiment 158.—Properties of Ferric Compounds.** *Materials:* Ferric chloride solution and the solutions used in Experiment 157.

To a little ferric chloride solution add (1) sodium hydroxide solution. The precipitate is ferric hydroxide. Describe it. Add to ferric chloride solution (2) a little solution of potassium ferricyanide. Compare the negative result with (2) in Experiment 157. Add as above (3) a little solution of potassium thiocyanate. The rich wine-red coloration is caused by the soluble ferric thiocyanate. This test distinguishes ferric from ferrous compounds. Add as above (4) a little solution of potassium ferrocyanide. The precipitate is ferric ferrocyanide. Describe it. Tabulate the results of these two experiments, showing the behavior of ferrous and ferric compounds under the same conditions.

**Experiment 159.—Reduction of Ferric Compounds.** *Materials:* Ferric chloride solution, zinc, hydrochloric acid.

Put a piece of zinc in ferric chloride solution made slightly acid by hydrochloric acid. The nascent hydrogen reduces the ferric to ferrous chloride. After the operation has proceeded for about fifteen minutes, test a portion of the liquid for a ferrous and a ferric compound by Experiments 157 (2) and 158 (3). If the tests are not conclusive, continue the reduction and test again. Describe the result.

**Experiment 160.—Oxidation of Ferrous Compounds.** *Materials:* Ferrous sulphate, hydrochloric acid, potassium chlorate, nitric acid.

(a) To a solution of fresh or freshly washed ferrous sulphate add a little hydrochloric acid, warm gently, and then add a few crystals of potassium chlorate. After heating a short time, test portions of the liquid for a ferric and a ferrous compound.

(b) Add 10 cubic centimeters of concentrated nitric acid, drop by drop, to a hot solution of ferrous sulphate to which a little sulphuric acid has been added, and boil. Test portions of the liquid for a ferric and a ferrous compound as in Experiment 159.

(c) Recall a third illustration of the oxidation of a ferrous to a ferric compound. Describe it briefly.

**Experiment 161.—Properties of Certain Iron Compounds.** *Materials:* Ferrous sulphate, hematite, limonite, magnetite, pyrite, siderite.

(a) Examine a crystal of ferrous sulphate, and state its most obvious properties. Heat it gently in a test tube inclined mouth downward. Describe the result. Test this crystal for ferrous and ferric compounds

## Experiments.

as in Experiment 159. State and explain the result. What is the common name of ferrous sulphate?

(b) Examine hematite, limonite, and magnetite, and state their properties. Draw the first two across a rough sheet of paper or a piece of ground glass, and describe the "streak" made by each. What is the formula of each compound? Prepare a hydrochloric acid solution of each and test for iron. State the result.

(c) Examine pyrite, and state its properties. It is iron disulphide. What is its formula? For what is it used? For what is it sometimes mistaken?

(d) Examine siderite, and state its properties. It is ferrous carbonate. What is its formula? Test a powdered specimen for a carbonate and for iron. State the result.

### Exercises for Review.

1. What happens when iron is (a) treated with acids, and (b) heated with sulphur?
2. Describe ferrous sulphide. What are formed by its interaction with warm hydrochloric acid?
3. What happens to iron when it is placed in copper sulphate solution?

### NICKEL AND COBALT.

#### **Experiment 162. — Test for Nickel.**

To a solution of nickel chloride add sodium hydroxide to alkaline reaction. The precipitate is nickelous hydroxide. Describe it.

#### **Experiment 163. — Test for Cobalt.** Repeat Experiment 102 (a).

### ORGANIC COMPOUNDS.

**Experiment 164. — Composition of Organic Compounds.** *Materials:* Turpentine, alcohol, camphor, kerosene, sugar, starch, flour, wood, paper, hair, candle, taper, gelatine, mustard, silver coin, red litmus paper, soda lime, porcelain dish, kerosene lamp, two bottles.

(a) *Carbon.* (1) Recall or repeat the experiments which showed that carbon is a constituent of wood, cotton, starch, sugar, illuminating gas and candle wax. (2) Heat a few drops of turpentine in a porcelain dish, and then set fire to it. Does it contain carbon? Hold a bottle over the flame long enough to collect any product, and then test

the contents for carbon dioxide with limewater; does the observation verify the previous conclusion? (3) Repeat (2) with alcohol. Does alcohol contain carbon? (4) Burn a small lump of camphor in a porcelain dish or on a block of wood. Does it contain carbon? (5) Hold a bottle over a burning kerosene lamp long enough to collect any product, and test as in (2). Does kerosene contain carbon?

(b) *Hydrogen*. (1) Set fire to a few drops of the following liquids in a porcelain dish, and hold over each flame a *cold* dry bottle long enough to allow the condensation of the water vapor, which is always one product of the combustion of organic compounds which contain hydrogen: alcohol, turpentine, kerosene. (2) Heat in separate test tubes the following dry solids, and if they contain hydrogen, a little water vapor will condense on the upper part of the test tube: sugar, starch, flour, wood, paper, hair. (3) Hold a cold, dry bottle for a few seconds over a burning kerosene lamp, a Bunsen flame, an ordinary gas flame, a burning candle, a burning taper, and describe the result. Is hydrogen a component of kerosene, illuminating gas, and wax?

(c) *Oxygen*, which unites with the hydrogen of organic compounds to form the water, may come from the compound, as in the case of sugar, starch, wax, wood, paper, or it may come from the air. No simple experiment will determine the source of the oxygen.

(d) *Nitrogen*. Mix a little granulated gelatine (one part) with dry soda lime (two parts) and heat the mixture in a test tube. Hold a piece of moist red litmus paper in the escaping vapor. It will be turned blue by escaping ammonia gas. Gelatine (also horn, glue, and leather) contains nitrogen, which is liberated in combination with hydrogen as ammonia gas.

(e) *Sulphur*. (1) Put a little mustard paste on a clean silver coin. The brown stain is silver sulphide. Explain. (2) Why is a silver spoon tarnished by a cooked egg?

Draw a general conclusion regarding the composition of organic compounds.

**Experiment 165.—Preparation and Properties of Alcohol.** (**Teacher's Experiment.**) *Materials:* Grape sugar, yeast, limewater, bone black, sodium hydroxide. The *apparatus* consists of a large bottle provided with a one-hole rubber stopper fitted with a delivery tube (like C, D, E, in Fig. 104) which reaches to the bottom of a small bottle; the latter has a two-hole stopper. The delivery tube passes

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through one hole, and through the other passes a bent tube connected with a U-tube.

I. Put a liter of water in the bottle, add 150 grams of grape sugar, and shake until dissolved; pour 150 cubic centimeters of yeast into this solution. Fill the small bottle half full of limewater. Fill the U-tube with pieces of sodium hydroxide. Connect the apparatus and stand it in a dark place, where the temperature is 25°–30° C.

Fermentation begins at once, and carbon dioxide — one of the products — bubbles through the limewater, which is protected from the action of the air by the sodium hydroxide. Examine the stopper for a leak, if no change occurs in the limewater. The operation should be allowed to continue at least a day, and longer if possible. The flask will then contain mainly water, unchanged grape sugar, alcohol, and some products of minor importance. Pour off the liquid, agitate it with a little bone black to remove the odor and color, and filter. The alcohol, which varies in quantity with the conditions, is dissolved in a large excess of water and must be separated by distillation.

II. The distillation is performed with the apparatus used in Experiment 13. Fill the flask half full of the liquid from I, add a few pieces of pipestem (or granulated zinc, or glass tubing) to prevent "bumping," and distil about 50 cubic centimeters. Save the distillate. Replace the residue in the flask by more liquid from I, distil again, and repeat this operation until all the liquid has been used. Replace the one-hole stopper with a two-hole stopper, insert a thermometer in one hole so that the bulb just touches the surface of the combined distillates, which should now be distilled. Heat gently, and collect in a separate receiver the distillate which is formed when the liquid boils between 80° and 93° C. This distillate contains most of the alcohol.

Test as follows: —

(a) Note the odor.

(b) Drop a little into a warm dish, and hold a lighted match over it. If it does not burn, it shows that the alcohol is too dilute. Put a little in a dish, warm gently, and light the vapor. Describe the result.

**Experiment 166.—Properties of Alcohol. (Optional.) Materials:** Alcohol, camphor, shellac, rosin, porcelain dish.

(a) Determine cautiously the odor and taste of alcohol. Drop a little on a glass plate or on a piece of paper, and watch it evaporate. Is its rate of evaporation more rapid than that of water?

(b) Weigh a measured quantity (about 25 cubic centimeters) of 95 per cent alcohol and calculate its specific gravity.

(c) Alcohol dissolves many organic substances. Try camphor, powdered shellac, or rosin. Describe the result. Verify the solvent power of alcohol by adding water to the solutions. Describe the result.

(d) Burn a little alcohol in a dish and observe the nature of the flame. What are the products of combustion?

**Experiment 167.—Preparation and Properties of Aldehydes.** *Materials:* Concentrated hydrochloric acid, ethyl alcohol, potassium dichromate solution, methyl alcohol, copper wire, forceps.

(a) *Acetic Aldehyde.* Add a little concentrated hydrochloric acid and several drops of ethyl alcohol to several cubic centimeters of potassium dichromate solution. Warm gently, and observe the peculiar-smelling gaseous product. It is aldehyde vapor, aldehyde itself being a colorless, extremely volatile liquid, which boils at 20.8° C.

(b) *Formic Aldehyde or Formaldehyde.* Put a few cubic centimeters of methyl alcohol in a test tube and stand the test tube in a rack. Wind a piece of copper wire into a spiral around a glass rod or lead pencil. Slip the spiral from the rod, grasp one end into the forceps, and heat the wire red-hot in the flame. Then quickly drop it in the methyl alcohol. The pungent vapor which is suddenly produced is largely the vapor of formaldehyde.

**Experiment 168.—Properties of Ether.** *Materials:* Ether, evaporating dish, glass plate, wax.

**Precaution.** *Ether vapor is easily ignited, and should never be brought near a flame.*

(a) Pour a little ether into a dish or test tube and observe the odor and volatility. Taste cautiously. Pour a drop upon a glass plate or a block of wood. How does its rate of evaporation compare with that of alcohol? Pour a little upon the hand and describe the result.

(b) Add a bit of wax to a few cubic centimeters of ether, and shake. The result is typical; draw a conclusion.

**Experiment 169.—Properties of Acetic Acid.**

Treat acetic acid as follows: —

(a) Taste (cautiously), and describe.

(b) Test with litmus paper, and describe the result.

(c) Warm a little in a test tube, and smell (cautiously). Describe the odor.

**Experiment 170.—Properties of Vinegar.**

(a) Show, experimentally, that vinegar contains acetic acid.

(b) Repeat Experiment 60, using vinegar instead of indigo solution.

**Experiment 171.—Test for Acetic Acid and Acetates.**

Cautiously add a few drops of concentrated sulphuric acid to equal (and small) volumes of acetic acid and alcohol. Shake and warm gently. The pleasant, fruitlike odor is due to the vapor of ethyl acetate, a volatile liquid which is always formed under these circumstances.

(NOTE. — This experiment is also a test for alcohol.)

**Experiment 172.—Preparation and Properties of Acetates.**  
*Materials for (a) :* Sodium carbonate, acetic acid, concentrated sulphuric acid, alcohol, porcelain (or agate) dish. *For (b) :* Litharge, acetic acid, porcelain dish.

Prepare one or both of the following acetates:—

(a) *Sodium acetate.* Dissolve 20 grams of sodium carbonate in 10 cubic centimeters of water in a porcelain (or agate) dish, and slowly add 30 cubic centimeters of commercial acetic acid, with constant stirring. If the solution is not acid, add a little more acetic acid. Filter the solution, if not clear. Evaporate to crystallization. When the crystals have formed, remove and dry them. Describe the crystals. Prove that they contain water of crystallization. Test the acetate as follows: (1) Dissolve a little in water, add a few drops of concentrated sulphuric acid, and boil. What does the odor show is present? What other acids have been similarly prepared? (2) Dissolve as in (1), add a few drops of alcohol and of sulphuric acid, and boil. What does the odor conclusively prove? Preserve the crystals, finally, in a glass-stoppered bottle, or in one having a cork covered with paraffin.

(b) *Lead acetate (poisonous).* To 10 grams of litharge add 18 cubic centimeters of commercial acetic acid in small portions. Stir the mixture constantly during the addition of acid. After all the acid has been added, heat gently until the action ceases. (If the solution is green or bluish, it is due to a copper compound. The copper may be precipitated and removed mechanically by standing a strip of lead in the solution for an hour or more. Pour off the clearer liquid and then filter.)

Evaporate cautiously to crystallization. Remove the crystals from the liquid, and dry at a moderate temperature. Preserve the crystals finally as in (a). Describe the crystals. Test them for lead (see Exp. 145 (b)), and for an acetate.

**Experiment 173. — Properties of Certain Organic Acids.** *Materials:* Tartaric and citric acids, potassium permanganate solution, sodium bicarbonate, sugar, concentrated nitric acid, evaporating dish, litmus paper.

(1) *Tartaric acid.* Observe and describe the results in the following: (a) Taste cautiously a dilute solution of tartaric acid. (b) Apply the litmus test. (c) Add a little of the solution to a sodium bicarbonate solution. (d) Dissolve two or three crystals of potassium permanganate in a test tube half full of water, add a little sodium hydroxide solution and two or three pieces of tartaric acid (solid). Warm gently, but do not shake. The change is due to the reduction of the potassium permanganate by the tartaric acid.

(2) *Citric acid.* Proceed as in (1) with citric acid.

(3) *Oxalic Acid.* (a) **This acid is poisonous. Do not taste it.** (b) and (c) Proceed as in (1). (d) Dissolve two or three crystals of potassium permanganate in a test tube half full of water and add half the volume of sulphuric acid. Add oxalic acid solution until a decided change appears. Describe and explain it. (e) Add a few drops of ink to oxalic acid solution, and shake. Describe the result.

**Experiment 174. — Preparation and Properties of Ethyl Acetate.**

Repeat Experiment 171.

**ANSWER :**

(1) What class of organic compounds does ethyl acetate represent ? What general property has this class ?

(2) To what inorganic compound does ethyl acetate correspond?

(3) What is the relation of ethyl acetate to (a) alcohol and (b) acetic acid ?

**Experiment 175. — Preparation of Soap.**

Prepare soap in an iron or a tin dish by one of the following methods :—

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(a) Dissolve 10 grams of sodium hydroxide in 75 cubic centimeters of water, add 30 grams of lard, and boil until the mixture begins to solidify. Then add 20 grams of fine salt in small portions. Stir constantly during the addition of the salt. Boil a few minutes. Let the mass cool, and then remove the soap, which will form in a cake at the surface.

(b) Dissolve 13 to 15 grams of sodium hydroxide in 100 cubic centimeters of water, add 100 cubic centimeters of castor oil, and boil for about half an hour. Add 20 grams of salt, and then proceed as in (a).

(c) Dissolve 8 grams of potassium hydroxide in 150 cubic centimeters of alcohol, add 10 grams of lard, and stir constantly while the mixture is being heated cautiously to sirupy consistency. Allow the solution to cool. The jellylike product is soap.

Preserve a sample.

**Experiment 176.—Properties of Soap.** *Materials:* Soap, sulphuric acid, calcium sulphate, magnesium sulphate, and acid calcium carbonate solutions.

Test as follows the soap prepared in Experiment 175:—

(a) Leave soap shavings exposed to the air for several days. What does the result show about the presence of water in the soap?

(b) Test soap solution with litmus paper.

(c) Add considerable dilute sulphuric acid to a soap solution. The precipitate is a mixture mainly of palmitic and stearic acids. Describe it.

(d) To a little soap solution in separate test tubes add calcium sulphate and magnesium sulphate solutions. Describe the result. Boil for a few minutes and describe the result. Prepare a solution of acid calcium carbonate by passing carbon dioxide into limewater until the precipitate is redissolved (see Exp. 69). Add some of the solution to a soap solution, and describe the result. Boil, as above, and describe the result.

**ANSWER :**

(1) What is hard water? Soft water?

(2) What is permanent hardness? Temporary hardness? How can the latter be removed?

**Experiment 177.—Properties of Glycerine.**

(a) Add a little glycerine to a test tube half full of water, and shake. Add considerable more glycerine, and shake. What does the result show about the solubility of glycerine in water?

(b) *Cautiously taste the liquid resulting from (a).* Describe the result.

**Experiment 178.—Fehling's Test for Sugar.** *Materials:* Copper sulphate, Rochelle salt, sodium hydroxide, and grape sugar solutions.

Mix equal (and small) volumes of copper sulphate, Rochelle salt, and sodium hydroxide solutions in a test tube, and boil carefully. The mixture should be strongly alkaline. Add a little grape sugar solution, and boil until a decided change is produced. The precipitate is cuprous oxide. Describe it.

(*NOTE.*—Cane sugar must be changed to grape sugar by boiling with dilute sulphuric acid before the above test is applicable.)

#### Exercises for Review.

1. What happens to sugar and starch (a) when heated, and (b) when treated with concentrated sulphuric acid?
2. What is the test for starch?
3. Discuss the solubility of alcohol in water.
4. What is the effect of heat upon paper and cotton? Of potassium permanganate on paper?

#### Experiment 179.—Properties of Benzene.

Put *one or two drops* of benzene in an evaporating dish, and *cautiously* bring a lighted match near it. Describe the result.

### LABORATORY EQUIPMENT.

The Equipment of a laboratory should be limited solely by the means at the disposal of the teacher. Accurate and rapid work is largely determined by the available facilities, and no pains should be spared to secure the equipment which will yield the largest educational return for the time and money expended.

The lists given below include the apparatus and chemicals needed for the experiments in this book. Quantities and prices have been omitted in justice to teachers, dealers, and the author. Different teachers use different quantities, prices fluctuate, and qualities vary. The author, at his own suggestion, has lodged with the L. E. Knott Apparatus Co., 16 Harcourt Street, Boston, Mass., information regarding the quantities

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of apparatus and chemicals used by his classes. It is hoped that teachers will correspond with both author and dealer when preparing order lists. The author takes this opportunity to say that he has no financial connection whatever with any dealer in scientific supplies.

### LIST A.—INDIVIDUAL APPARATUS.

This list includes the apparatus constantly used by a single student, who should be provided with each piece. The set will cost from \$4.75 to \$5. The discount on apparatus in this and succeeding lists depends upon the total amount of the order.

6 Test tubes, 6 x $\frac{1}{4}$ .	1 Mortar and pestle, 3 in.
3 Test tubes, 8 x 1.	1 Deflagrating spoon.
1 Test-tube holder.	1 Pneumatic trough.
1 Test-tube rack.	2 ft. Rubber tubing, $\frac{1}{4}$ in. in diam.
1 Test-tube brush.	100 Filter papers, 4 in.
1 Bunsen burner.	1 ft. Glass rod.
1 Blowpipe.	6 in. Rubber tubing, $\frac{1}{4}$ .
1 Blowpipe tube.	1 One-hole and 1 two-hole rubber stopper to fit large test tube.
5 Bottles, wide mouth, 250 cc.	4 ft. Glass tubing to fit rubber stoppers (above).
1 Funnel, 2 $\frac{1}{2}$ in.	1 Safety tube.
1 Evaporating dish.	
1 Pair iron forceps.	
1 Triangular file.	

### LIST B.—SPECIAL APPARATUS.

This list includes apparatus used occasionally. Numbers in parentheses refer to experiments. The set will cost from \$3 to \$3.25.

1 Crucible, Hessian, 4 in. deep (59, 90).	1 Graduated cylinder, 25 cc. (25 and others).
1 Dish, lead (80).	1 Magnet (156).
1 Flask, Erlenmeyer, 250 cc. (25).	1 Candle (63, 77).
1 Pinchcock, Mohr (96).	1 Sand-bath pan, 4 in.
1 Screw, Hofmann (25).	1 Wing-top burner (Int. § 3(δ)).
1 Thistle tube (96).	1 Dish, iron or tin (109, 111).
1 Lamp chimney (77).	1 Retort, 250 cc. (49).

## LIST C.—APPARATUS FOR TEACHER'S EXPERIMENTS.

This list includes the additional apparatus for the Teacher's Experiments. Numbers in parentheses refer to experiments. The set will cost about \$11.

Electrolysis apparatus (22, 36).	1 Safety tube (10).
Flask, 500 c.c. (10, 13, 165).	1 Condenser complete (13, 165).
Two-hole rubber stopper for above.	1 Tripod (13).
U-tube (10, 73, 165).	1 Thermometer (165).
2 One-hole rubber stoppers for above.	1 Chlorine tube (23).
4 in. Capillary tubing (10, 22, 36).	1 Ignition tube, 6 in. (73).
3 ft. Glass tubing to fit rubber stoppers.	1 Bottle, wide mouth, 50 cc. (10). Battery, 3 cells (Grenet) (22, 36, 37). 1 Bottle, 2000 cc. (165).

## LIST D.—GENERAL APPARATUS.

This list includes the general laboratory apparatus. It should be extended as demands arise. It does not include such items as duplicate stoppers, extra glassware, tools, etc. Special inexpensive articles are noted in the experiments and in the "Handbook for Teachers" accompanying this book.

Corks, assorted.	Sand.
Copper wire, No. 20.	Wood, thin sticks (Exp. 6 and others).
Glass plates, 4 × 4 in.	Rule, foot and 30 cm.
Iron stands, 3 rings, 2 clamps.	Scales, trip.
Matches.	Weights for above.
Wire gauze, iron, 4 × 4 in.	Tapers.
Wooden blocks, 6 × 6 × 1 in., 6 × 6 × $\frac{1}{4}$ in., 4 × 4 × $\frac{1}{2}$ in. (with $\frac{1}{2}$ in. hole in center—see Exp. 38).	Emery paper. Kerosene lamp. Graduated cylinders, 500 cc., 100 cc.

## LIST E.—CHEMICALS.

This list includes the chemicals needed for this book. Numbers in parentheses refer to experiments in which the chemicals are used.

Acid, acetic.	Acid, hydrochloric.
citric.	nitric.

## Experiments.

Acid, oxalic.	Coin (silver).
pyrogallic (25).	Copper nitrate.
sulphuric.	sheet.
tartaric.	sulphate (cryst.).
Alcohol, ethyl.	Cotton (absorbent).
methyl (167).	Cream of tartar.
Alum, chrome.	Ether.
potassium.	Galena (148).
Aluminium, metal.	Gelatine.
sulphate.	Glycerine.
Ammonium, chloride.	Gold leaf (book).
hydroxide.	Hematite (161).
nitrate.	Indigo.
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Siderite (161).	sheet.
Silver nitrate.	sulphate.
Soap.	

## SOLUTIONS.

The following solutions are needed for the experiments in this book  
 Those not included are described in the experiments requiring their use

## Experiments.

Alum, 10 per cent.	Magnesium sulphate, 10 per cent.
Ammonium chloride, 10 per cent.	Manganese chloride, 10 per cent.
Ammonium hydroxide, 1 vol. to 3 vols. water.	Mercuric chloride, 5 per cent. Pot son.
Ammonium oxalate, <sup>1</sup> 4 per cent.	Mercurous nitrate, <sup>2</sup> 5 per cent.
Ammonium sulphide, 1 vol. to 1 vol. water.	Nitric acid, 1 vol. to 4 vols. water.
Barium chloride, <sup>3</sup> 5 per cent.	Potassium bromide, 5 per cent.
Battery solution (Grenet). Dissolve 103 gm. powdered potassium dichromate in 1 liter of water and slowly add 103 gm. conc. sulphuric acid with constant stirring.	Potassium chloride, 5 per cent.
Calcium chloride, 10 per cent	Potassium chromate, 10 per cent.
Chlorine water, <sup>1</sup> saturated (see Exp. 23, 38).	Potassium dichromate (or bichromate), 5 per cent.
Cobalt nitrate, 5 per cent.	Potassium ferricyanide, 10 per cent.
Cochineal. Prepare as described under Indigo.	Potassium ferrocyanide, 10 per cent.
Copper sulphate, 10 per cent.	Potassium hydroxide, 10 per cent.
Disodium phosphate, 10 per cent.	Potassium iodide, 5 per cent.
Ferric chloride, 5 per cent.	Potassium nitrate, 10 per cent.
Ferrous sulphate, <sup>1</sup> 10 per cent.	Potassium permanganate, <sup>2</sup> 5 per cent.
Hydrochloric acid, 1 vol. to 4 vols.	Potassium sulphate, 10 per cent.
Indigo. Grind a little with water and dilute as desired.	Potassium thiocyanate (or sulphocyanide), 1 per cent.
Iodine. Grind to solution 12 gm. iodine, 20 gm. potassium iodide, 10 cc. water, and add to 1000 cc. water.	Silver nitrate, 5 per cent.
Lead acetate, 10 per cent.	Sodium carbonate, 10 per cent.
Lead nitrate, 10 per cent.	Sodium chloride, 10 per cent.
Limewater. Let water stand over lime for several days, and siphon off the clear liquid.	Sodium hydroxide, 10 per cent.
	Stannous chloride. <sup>1</sup> Dissolve 500 gm. of the salt in 1000 cc. hot conc. hydrochloric acid, and add a piece of tin.
	Sulphuric acid, 1 vol. to 4 vols. water.
	Tartar emetic, 10 per cent.
	Zinc sulphate, 10 per cent.

<sup>1</sup> Must be freshly prepared.<sup>2</sup> Use distilled water.<sup>3</sup> Use distilled water, and add 75 cc. concentrated nitric acid and a little mercury.

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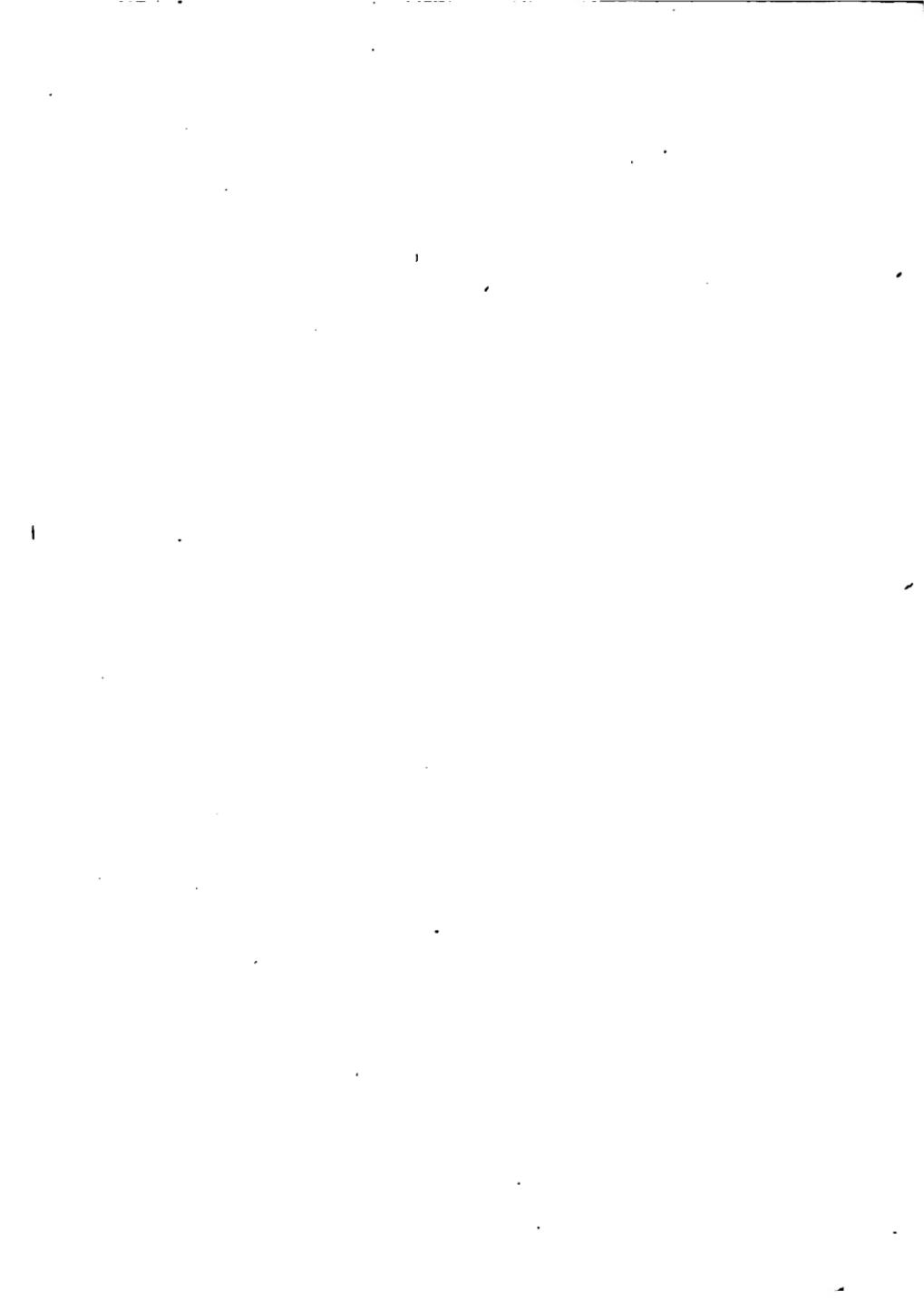
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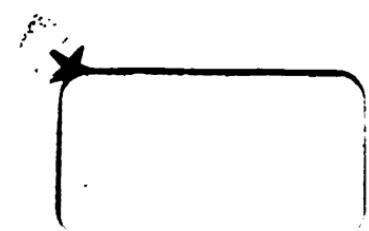
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